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Volume 3. Sessions 7 and 8

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Desulfurization	Economics	Clean Coal
Sulfur Dioxide	Sorbents	Acid Rain
Scrubbers	Wastes	Spray Drying
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PREFACE

The First Combined FGD and Dry SO₂ Control Symposium was held in St. Louis, Missouri, October 25 - 28, 1988. This Symposium, jointly sponsored by EPRI and EPA, had as its objective the exchange of technical and regulatory information on sulfur oxide control technology, including wet and dry scrubbers, emerging processes, and international developments in clean coal/acid rain technologies.

Eighty-five papers were presented by EPA and EPRI staff members, representatives of utility companies, equipment manufacturers, research and development companies, and university researchers. Specific topics discussed in symposium presentations included: retrofit economics, spray dryer technology, furnace sorbent injection topics (demonstration results, byproduct utilization, enhancements), wet FGD operation, municipal solid waste facilities, and post-combustion dry technologies. Also included were concurrent sessions on special topics of interest, including dry FGD, new technologies, and FGD improvement.

The Proceedings of this Symposium have been compiled in three volumes. Volume 1 contains papers from the following sessions:

- Session 1: International Overview
- Session 2: Retrofit Economics
- Session 3: Spray Dryer Technology
- Sessions 4A/4B: Furnace Sorbent Injection - Demonstrations/
Integration/Byproduct Utilization

Contained in Volume 2 are papers presented in these sessions:

- Sessions 5A/5B: FSI Impacts/Enhancements/Wet FGD Operation
- Session 6: Municipal Solid Waste Facilities

Contained in Volume 3 are papers presented in these sessions:

- Sessions 7A/7B/7C: Special Topics: Dry FGD Fundamentals/New
Technologies/FGD Improvement
- Session 8: Post-Combustion Dry Technologies

The assistance of Holly Rossi, Radian Corporation, in preparing for the Symposium and in compiling these Proceedings is gratefully acknowledged.

CONTENTS

VOLUME 1

<u>Paper</u>		<u>Page</u>
SESSION 1: INTERNATIONAL OVERVIEW Chairman, J. Abbott, EPA		
1-1	"FGD Research and Development Status in the U.S.," D. Delleney and J. Dickerman	1-1
1-2	"A Programme for Reducing SO ₂ Emissions from UK Power Stations - Present and Future," W. Kyte	1-14
1-3	"Progress in European SO _x /NO _x Control," B. Forck	1-21
1-4	"Progress in European SO ₂ and NO _x Emission Control," W. Ellison and H. Weiler	1-38
1-5	"Flue Gas Cleaning in Dutch Power Stations," F. van der Bruggen and J. Koppius-Odink	1-66
1-6	"Recent Developments in SO ₂ and NO _x Abatement Technology in Japan and Far Eastern Countries," J. Ando and N. Kaplan	1-91
SESSION 2: RETROFIT ECONOMICS Chairman, P. Radcliffe, EPRI		
2-1	"The Design, Operation, and Performance of Current Generation Retrofit FGD Systems on Coal-Fired Utility Boilers," B. Laseke ..	2-1
2-2	"Site-Specific Evaluation of Six Sorbent Injection Processes," W. Frazier, P. Ireland, G. Brown, and P. Radcliffe	2-20
2-3	"Lime/Limestone FGD and Sorbent Injection Technology Retrofit Difficulty at 60 Coal-Fired Utility Power Plants," T. Emmel and N. Kaplan	2-38
SESSION 3: SPRAY DRYER TECHNOLOGY Chairman, R. Glover, EPRI		
3-1	"Results from the TVA 10-MW Spray Dryer/ESP Evaluation," C. Brown, G. Blythe, L. Humphries, R. Robards, R. Runyan, and R. Rhudy	3-1
3-2	"The GRDA Unit No.2 Dry FGD System: Performance and Operating Experience," J. Buschmann, T. Lillestolen, J. Mills, and J. Marcy	3-21

CONTENTS (Continued)

<u>Paper</u>	<u>Page</u>
3-3 "Evaluation of a Combined $\text{Ca}(\text{OH})_2/\text{NH}_3$ Spray Dryer System for SO_2 Removal on High Sulfur Coal," W. Davis, G. Reed, A. Pakfasi, G. Smith, and T. Keener	3-42
3-4A "Update of Joy/Niro U.S. Utility Spray Dryer FGD Systems," J. Donnelly, M. Quach, S. Wolf, and G. Fosher	3-56
3-4B "Update on Spray Dryer FGD Experience in Europe and in the People's Republic of China," K. Felsvang, R. Hahn, P. Necker, M. Novak, Y. Qing, N. Raffelsberger, E. Schumacher, H. Spannbauer	3-73
3-5 "Results from EPRI High Sulfur Spray Dryer Pilot Tests," G. Blythe, L. Lepovitz, R. Rhudy	3-94
SESSION 4A: FURNACE SORBENT INJECTION - DEMONSTRATIONS Chairman, R. Stern, EPA	
4A-1 "Operation of the LIMB/Humidifier Demonstration Unit at Edgewater (104 MWe), P. Nolan, R. Hendriks, and N. Kresovich	4-1
4A-2 "Prototype Evaluation of Dry Sorbent Injection with Humidification," G. England, B. Folsom, R. Payne, T. Sommer, J. Chappell, M. McElroy, and I. Huffman	4-15
4A-3 "Development and Demonstration of Sorbent Injection for SO_2 Control on Tangentially Coal-Fired Boilers," M. Gogineni, J. Clark, R. Koucky, J. Marion, D. Anderson, A. Kwasnik, E. Gootzait, D. Lachapelle, and S. Rakes	4-35
4A-4 "Status of the LIFAC SO_2 and NO_x Removal Process," T. Kenakkala	4-51
4A-5 "Sorbent Slurry Injection for SO_2 Control," R. Mangal, M. Mozes, R. Thampi, and D. Tubman	4-66
4A-6 "Desulfurization Results for Three Different Firing Concepts," M. Chughtai	4-88
4A-7 "Austrian Experience with Furnace Limestone Injection," G. Staudinger, P. Melcher, and K. Eckerstorfer	4-109
4A-8 "Four Years of Operating Experience with Direct In-Furnace SO_2 Reduction at 600 MWe Unit of Provence Power Station," M. Vandycke, B. Auric, and J. Merry	4-121

CONTENTS (Continued)

<u>Paper</u>	<u>Page</u>
SESSION 4B: INTEGRATION/BYPRODUCT UTILIZATION Chairman, M. McElroy, EPRI	
4B-1 "Improving Sludge Dewatering in Magnesium-Enhanced Wet Lime FGD Systems," L. Benson, R. D'Alesandro, J. Wilhelm, and A. Randolph	4-135
4B-2 "Recycle/Reuse of Boiler Chemical Cleaning Wastes in Wet Limestone FGD Systems," M. Stohs, D. Owens, and W. Micheletti ...	4-151
4B-3 "Design of Waste Management Systems for Furnace Sorbent Injection Technologies," G. Guntz, M. Lees, D. Saylor, and D. Golden	4-169
4B-4 "Environmental Assessment of an FGD Sludge Disposal Site," I. Murarka and D. Rai	4-189
4B-5 "Spray Dry Absorption-Oxidation of SO ₂ /NO _x ," A. Stromberg and H. Karlsson	4-204
4B-6 "Technology Development Status of Nitric Oxide Abatement Using Ferrous Chelates," D. Zabcik	4-224
4B-7 "Experiences with Active Coke Processes for Simultaneous Removal of SO ₂ and NO _x ," E. Richter, K. Knoblach, and W. Wunnenberg	4-229
4B-8 "Simultaneous NO _x /SO ₂ Removal with Dry Sorbent Injection," M. Teague, R. Thompson, and L. Muzio	4-247

CONTENTS

VOLUME 2

<u>Paper</u>		<u>Page</u>
SESSION 5A: FSI IMPACTS/ENHANCEMENTS		
Chairman, D. Drehmel, EPA		
5A-1	"Design and Operation of Feeding Systems for High Reactivity Sorbents," P. Solt	5-1
5A-2	"Field and Laboratory Measurements of Fly Ash Properties and Precipitator Performance Parameters with Furnace Sorbent Injection," G. Faulkner, G. Marchant, Jr., E. Landham, Jr., and J. DuBard	5-13
5A-3	"The Radox Project - A Summary Review," G. DeMichele	5-33
5A-4	"Mechanistic Studies of Sorbent Utilization Enhancement by Humidification," R. Dahlin and R. Beittel	5-55
5A-5	"Rate Controlling Processes in Humidification for Duct SO ₂ Capture," J. Kramlich, D. Moyeda, G. Newton, and R. Payne ²	5-71
5A-6	"Pilot Plant Evaluation of Post-Combustion LIMB SO ₂ Capture," C. Sedman, D. Drehmel, J. Chang, and C. Jorgensen	5-91
5A-7	"Effect of CaO Sorbent Physical Parameters Upon Sulfation," B. Gullett and K. Bruce	5-103
5A-8	"Laboratory and Commercial-Scale Results of Testing Surfactant-Modified Sorbents," D. Kirchgessner, W. Jozewicz	5-121
SESSION 5B: WET FGD OPERATION		
Chairman, R. Moser, EPRI		
5B-1	"Results of Wet FGD Tests at EPRI's High Sulfur Test Center," J. Burke, S. Gray, R. Moser	5-136
5B-2	"Advanced Simplified Wet FGD Designs," S. Dalton, R. Moser, D. Colley, and J. Burke	5-166
5B-3	"Corrosion Control in SO ₂ Scrubbers by Impressed Current," G. Koch, S. Pednekar, and B. Syrett	5-183
5B-4	"Development of a Predictive Model for Limestone Dissolution in Wet FGD Systems," J. Jarvis, F. Meserole, T. Selm, G. Rochelle, and R. Moser	5-192

CONTENTS (Continued)

<u>Paper</u>	<u>Page</u>
5B-5 "Performance Impact of Mist Eliminators and Wet Electrostatic Precipitators," E. Bakke and O. Sarmiento	5-216
5B-6 "Video Based In-Situ Droplet Concentration and Size Analyzer," J. McCain	5-230
5B-7 "Guidelines for Troubleshooting Utility Mist Elimination Systems," F. Jones, D. Colley, D. Balfour, R. Rhudy, and R. Keeth	5-244
5B-8 "Guidelines for Troubleshooting Excessive Stack Opacity," D. Balfour, R. Rhudy, R. Keeth	5-263
SESSION 5B: WET FGD OPERATION (Continued) Chairman, C. Dene, EPRI	
5B-9 "Performance and Operating Costs of the Somerset Wet Limestone FGD System," D. McCoy, B. Koch, W. Rogers, H. Crosby, and J. Smigelski	5-278
5B-10 "FGD Reliability Improvement at LG&E: Cane Run 6 Case Study and Overall Project Status," C. Weilert, D. Froelich, and M. Schmitt	5-293
5B-11 "Inhibited Sulfite Oxidation by Thiosulfate in Wet Lime/Limestone FGD Processes: Results of Laboratory Studies and Testing at EPRI's High Sulfur Test Center Mini-Pilot," D. Owens, G. Maller, F. Meserole, R. Chin, G. Rochelle, and R. Moser	5-310
5B-12 "Control and Reduction of Gypsum Scale in Wet Lime/Limestone FGD Systems by Addition of Thiosulfate: Summary of Field Experiences," R. Moser, D. Owens, and D. Colley	5-335
5B-13 "Design, Startup, and Operating Experience of FGD System with Gypsum Byproduct at Reidersbach No. 2 in Austria," P. Kneissl, G. Staudinger, and M. Weitzer	5-355
5B-14 "Simultaneous SO ₂ and Particulate Removal in a Jet Bubbling Reactor," R. Sherwin, B. Gilbert, K. Kitamoto, Y. Yamaguchi, Y. Ogawa, and H. Koshizuka	5-379
5B-15 "The Bischoff Flue Gas Desulfurization Process," P. Kutemeyer and K. Hegemann	5-399
5B-16 "Operating Experience with Advanced FGD Technology in West Germany," M. Schutz, J. Glamser, and M. Eikmeier	5-416

CONTENTS (Continued)

<u>Paper</u>		<u>Page</u>
	SESSION 6: MUNICIPAL SOLID WASTE FACILITIES Chairman, T. Brna, EPA	
6-1	"A Comparison of HCL, SO ₂ , and Particulate Emissions from Three Different MSW Solid Waste-Fired Boilers," M. Sandell, V. Petti, and T. Porter	6-1
6-2	"Dry Scrubbing Process for Waste-To-Energy Applications-- Operating Experience and Performance Data," P. Dhargalkar	6-19
6-3	"Characterization of Emissions for a Municipal Solid Waste Incinerator with a Dry Scrubber," T. Brna, C. Sedman, and C. Riley	6-31
6-4	"Operating Experience with a Spray Dry Scrubbing System on an RDF-Fired Boiler," G. Bresowar, D. Collins, and J. Accortt	6-53

CONTENTS

VOLUME 3

<u>Paper</u>	<u>Page</u>
SESSION 7: SPECIAL TOPICS	
SESSION 7A: DRY FGD FUNDAMENTALS	
Chairman: D. Mobley, EPA	
7A-1	"An Experimental and Theoretical Study of the Fundamentals of the SO ₂ /Lime Reaction at High Temperatures," D. Pershing, C. Milne, and D. Kirchgessner 7-1
7A-2	"Dry Injection - Kinetic Studies," I. Bjerle and A. Karlsson 7-21
7A-3	"Laboratory Tests on Flue Gas Desulfurization by Dry Limestone Injection," F. Mayrhuber and G. Staudinger 7-40
7A-4	"Surface Chemical Reactivity of Different Calcium Based Sorbents with SO ₂ ," D. Beruto, M. Giordani, R. Botter, G. Chiarello, A. Lumaichi, F. Parmigiani, P. Ghetti, and G. DeMichele 7-55
7A-5	"Dry Sorbent Recycle Processes," T. Lott, D. Teixeira, L. Muzio, and M. Teague 7-66
7A-6	"Calcium Hydroxide Reactivity with Sulfur Dioxide from X-Ray Diffraction Peak Profiles," F. Briden and D. Natschke 7-83
SESSION 7B: NEW TECHNOLOGIES	
Chairman, C. Sedman, EPA	
7B-1	"Test Results on the Use of a Circulating Fluidized Bed Absorber (CFBA) for Control of SO ₂ ," T. Keener, X. Jiang, and J. Jao 7-99
7B-2	"A Pilot Demonstration of the Limestone Emission Control (LEC) System," D. Furlong, J. Wright, and M. Prudich 7-105
7B-3	"SO ₂ Recovery by Sodium Phosphate Solution Scrubbing," O. Erga 7-125
7B-4	"The 3-S Process: Simultaneous (Acid Gas and NO _x) Sodium-Based Sorption of Waste Gases," R. Lindbauer and F. Maier 7-135
7B-5	"Production of Lime/Fly Ash Absorbents for Flue Gas Desulfurization," G. Rochelle and J. Peterson 7-143

CONTENTS (Continued)

<u>Paper</u>	<u>Page</u>
7B-6 "Physical and Chemical Activation of Fly Ash to Produce Reagent for Dry FGD Processes," H. Karlsson, T. Peterson, J. Peterson, and I. Bjerle	7-160
SESSION 7C: FGD IMPROVEMENT Chairman, M. Maxwell, EPA	
7C-1 "On-Line Electrochemical Corrosion Monitoring in a Flue Gas Heat Exchanger," D. Farrell, W. Cox, B. Syrett, and R. Keeth	7-180
7C-2 "The Evolution of Fluorelastomeric Coatings for Flue Gas Desulfurization," K. Brethauer and J. Montle	7-199
7C-3 "Life-Cycle Cost Model for FGD Components," J. Redmond, Y. Shah, V. DiGirolamo, and W. Plant	7-217
7C-4 "Performance of Linings in FGD Systems," H. Rosenberg, G. Koch, C. Kistler, Jr., W. Mueller, and P. Radcliffe	7-233
7C-5 "FGD Chemistry Video Series," N. Gates and R. Moser	7-252
7C-6 "Chemical Additives for Dry FGD Scrubbers," L. Lin, R. Shiely, E. Ekis, Jr., and M. Meyerkord	7-255
SESSION 8: POST-COMBUSTION DRY TECHNOLOGIES Chairman, R. Rhudy, EPRI	
8-1 "Full Scale Demonstration of Additive NO ₂ Reduction with Dry Sodium Desulfurization," J. Hammond	8-1
8-2 "In-Duct Scrubbing Technologies for SO ₂ Control," C. Drummond ...	8-24
8-3 "Technical and Economic Evaluation of HYPAS," D. Giovanni and R. Rhudy	8-75
8-4 "Operating Experience with a Dry FGD Plant Using a Circulating Fluid Bed (CFB) at the Lignite-Fired Power Station of PREAG in Borken, Federal Republic of Germany," H. Sauer	8-97
8-5 "Scale-Up Testing of the ADVACATE Damp Solids Injection Process," J. Chang, C. Sedman, and T. Pearson	8-122
8-6 "Dry Flue Gas Desulfurization Process Using Absorbent Made from Fly Ash," M. Narita, S. Kudo, T. Veno, N. Arashi, T. Nishimura, and T. Mizoguchi	8-139

CONTENTS (Continued)

<u>Paper</u>	<u>Page</u>
8-7 "Hydrate and Process Parameters Controlling SO ₂ Removal During Hydroxide Injection Near 1000°F," S. Bortz, V. Roman, and G. Offen	8-156
8-8 "E-SO ₂ Studies Pilot Evaluation," L. Hovis, R. Valentine, B. Jankura, P. Chu, and J. Chang	8-177
UNPRESENTED PAPERS	
"The Ecotech Dry Scrubber--for the Simultaneous Dry Scrubbing of High Temperature Hard Particulate Matter, Condensable Solids, and Noxious Gases Entrained in a Gas Stream," J. Chambers	U-1
"SO ₂ Capture in a Coal-Fueled Gas Turbine System, S. Johnson, L. Walkauskas, and J. Morency	U-18
"FGD System Cost Comparisons," C. Gaige, S. Smith, R. Norton, and P. Dyer	U-38
"Combined SO ₂ /NO _x Removal in a High-Sulfur Spray-Dryer/Fabric-Filter System," D. Livengood, H. Huang, J. Allen, and P. Farber	U-43
Appendix A - List of Attendees	A-1

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

SESSION 7A: DRY FGD FUNDAMENTALS

Chairman, J. David Mobley, EPA/AEERL

AN EXPERIMENTAL AND THEORETICAL STUDY OF THE FUNDAMENTALS

OF THE SO₂/LIME REACTION AT HIGH TEMPERATURES

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ABSTRACT

An experimental and theoretical study of the SO₂/lime reaction is described. The experimental portion focuses on elucidating the differences in reactivity between Linwood calcium hydrate and Linwood calcium carbonate at high temperatures (1250 to 1450 K) and at short times (30 ms). The contributions of particle size effects to reactivity differences are examined using air classified sorbents. The impact of temperature and SO₂ partial pressure on sorbent utilization is also determined. The experimental results indicate that the primary reason for the superior reactivity of hydrates relative to carbonates is the smaller particle diameter of the hydrates.

Based on the experimental results, a comprehensive, mathematical SO₂-sorbent reaction model was developed which includes simultaneous calcination, sulfation, and sintering. The model is unique relative to previous efforts because it begins with the raw material and calculates subsequent surface area and pore size properties for the simultaneously calcining and sulfating particles.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Growing public concern over the effects of acid rain has stimulated interest in the SO₂/lime reaction as a means of reducing SO₂ emissions using calcium-based sorbents. The reaction of SO₂ with calcium-based sorbents to form CaSO₄ is a complex, heterogeneous process. The process begins with the calcination of limestone or hydrated lime to form CaO. This porous, active lime subsequently

suffers the competitive processes of sintering (which involves grain growth and results in a less active, lower surface area CaO) and sulfation in the presence of oxygen to yield CaSO_4 .

The overall objectives of this research were to develop an experimental and theoretical understanding of the SO_2 /lime reaction, with particular attention being given to the differences in reactivity between hydrates and carbonates and to modeling the simultaneous calcination and sulfation of raw sorbents.

The modeling efforts which have been attempted heretofore, for example, the grain models of Pigford and Sliger (1973), Hartman and Coughlin (1976), and Georgakis, Chang, and Szekely (1979), and the pore models of Ramachandran and Smith (1977), Simons and Rawlins (1980), Bhatia and Perlmutter (1981), and Christman and Edgar (1983), have not started with the raw sorbent material and have not considered its simultaneous calcination, sintering, and sulfation in a comprehensive model.

SORBENT ACTIVATION FUNDAMENTALS

High resolution scanning electron microscope (SEM) photographs were obtained for both the flash calcined and oven calcined sorbents used in the experiments to develop a physical picture of the development of porous CaO and its subsequent sintering processes. Linwood hydrate and carbonate were oven calcined in an air-purged electric muffle furnace. Their appearance is that of nonuniform grains which have been joined together by necks to form a continuous porous matrix. Prolonged periods of sintering (15 hours at 1073 K) increase the size of the grains, a result which corroborates nitrogen adsorption data that indicate a decrease in surface area from 11 to $3.7 \text{ m}^2/\text{g}$. The appearance of materials flash calcined at 1370 K is somewhat different. Little internal porosity is visible and the grain sizes are much smaller. The grains also have a plate-like appearance. However, the basic structure of flash calcined CaO appears to be that of a porous matrix of interconnected grains and/or plates.

MODEL CONCEPT AND MATHEMATICAL DEVELOPMENT

The porous matrix of interconnected grains revealed by the SEM photomicrographs can be approximated by overlapping spheres as described by Lindner and Simonsson (1981). This overlapping grain model simulates sintering by moving the grain centers closer together. Figure 1 shows the overlapping spheres concept with part of the center sphere cut away to show the radial distances r and r_i . The sphere radius is r and the radial distance to the plane of contact between two spheres is r_i . For a system of overlapping spherical grains with n contacts per grain, the grain surface area (S_g) and volume (V_g) are

$$S_g = 4\pi r \left[1 - \frac{n}{2} \left(1 - \frac{r_i}{r} \right) \right] \quad (1)$$

and

$$V_g = \frac{4}{3} \pi r^3 \left\{ 1 - \frac{n}{4} \left[2 - 3 \frac{r_i}{r} + \left(\frac{r_i}{r} \right)^3 \right] \right\}. \quad (2)$$

To describe overall particle properties, Lindner and Simonsson introduce the number density of grains N to give

$$S = NS_g \quad (3)$$

and

$$1 - e = NV_g, \quad (4)$$

where S is the surface area per particle volume and e is the porosity. Substitution of Eqns. 1 and 2 into Eqns. 3 and 4 gives a system of two equations and two unknowns, r and r_i . The nonlinear equations are solved by the Newton-Raphson method.

SINTERING MODEL

The sintering of grains at high temperatures is driven by the capillary forces associated with the curvature of surfaces. By diffusion or viscous flow processes, material is transferred to the grain neck area. The sintering process influences particle surface area and porosity. One indication of the extent of sintering is surface area loss. The surface area may be expressed as a function of time, temperature, and various gas concentrations that catalyze sintering. In the case of CaO in a combustion environment, these gases include H_2O and CO_2 (Borgwardt, Roache, and Bruce, 1986; Anderson, Horlock, and Avery, 1965).

A fundamental understanding of the sintering of CaO under sorbent injection conditions is not available and a theoretical model of the process does not exist. Therefore, the sintering model developed herein is based on a consistent set of empirical relations that mathematically describe trends seen in the available data. In this empirical sintering model the rate of surface area loss is proportional to the square of the difference between the actual surface area and the equilibrium surface area that the particle reaches after long sintering times. This model was formulated by Silcox, Kramlich, and Pershing (1988) and was used to correlate the data of Borgwardt, Bruce, and Blake (1985).

The Silcox rate equation is modified to correspond with the recent data of Borgwardt (1988 a and b) and includes the effects of both H_2O and CO_2 :

$$\frac{dS_m}{dt} = -2450 \left(1 + 50.7 p_{H_2O}^{0.17} + 10.3 p_{CO_2}^{0.67} \right) \exp\left(\frac{-29600}{T}\right) (S_m - 5000)^2 \quad (5)$$

Eqn. 5 is based on data obtained at a maximum temperature of 1273 K. Sintering data at temperatures of practical interest are almost unknown so Eqn. 5 is used to extrapolate sintering rates to higher temperatures.

CALCINATION MODEL

The calcination model utilizes an empirical modification of the

shrinking-core model. The shrinking-core model, in which chemical reaction controls and the rate of reaction is proportional to the surface area of the unreacted core, gives the relation

$$x = 1 - \left(1 - \frac{k}{r_0} t\right)^3 \quad (6)$$

where x is conversion, k is the rate constant, r_0 is the initial radius of the grains within the particle, and t is time. The initial grain radius r_0 is estimated from the raw sorbent surface area S_{m0} as

$$r_0 = \frac{3}{\rho S_{m0}} \quad (7)$$

where ρ is the density of CaCO_3 or Ca(OH)_2 . However, an examination of available calcination data suggests that Eqn. (6) be empirically modified to

$$x = 1 - \left(1 - \frac{k}{d_0^{0.6}} t\right)^3 \quad (8)$$

where d_0 is the initial particle diameter (m).

The rate constant k in Eqn. 8 for CaCO_3 is

$$k = 10.303 \exp\left(\frac{-10980}{T}\right), \text{m}^{0.6}/\text{s} \quad (9)$$

and is based on the high temperature data of Borgwardt (1985). Based on Eqn. 8 and the data of Bortz and Flament (1985), the rate constant for hydrate calcination is estimated as

$$k = 53.87 \exp\left(\frac{-8300}{T}\right), \text{m}^{0.6}/\text{s}. \quad (10)$$

For boiler injection temperatures, this rate constant predicts nearly instantaneous calcination.

A comparison of the combined calcination and sintering model to the data of Roman, et al. (1986) is shown in Figure 2 for Marianna limestone calcined at 1373 K in an isothermal flow reactor. The over-prediction of the measured surface areas may be due to sintering and recarbonation in the sample collection system.

To connect the calcination model to the sulfation model discussed below, an overall conceptual model for the calcining particle is required. The particle model presented herein represents a hydrate or carbonate particle as a sphere that decomposes by the shrinking-core mechanism. A porous outer shell of high surface area

CaO grains is produced as illustrated in Figure 3. The CaO grains are modeled as overlapping spheres. The porosity of the calcined shell is estimated by the theoretical porosity attributed to the parent material [54 percent for CaCO_3 and 49 percent for Ca(OH)_2] and the initial porosity of the sorbent. The initial surface area of the freshly calcined CaO grains is assumed to be $100 \text{ m}^2/\text{g}$ for the dispersed systems under consideration. As calcination proceeds, concentric shells of CaO are produced, each with a different grain size.

SULFATION FUNDAMENTALS

SULFATION MODEL

Each shell of CaO in the particle model is allowed to react with SO_2 , as soon as it is formed, while it simultaneously sinters. The rate of sulfation is limited by product-layer diffusion, which is influenced by surface area, grain overlap, and product-layer thickness. Sulfation is also limited by gas-phase diffusion to the particle surface and pore diffusion through the particle, which is dependent on porosity and mean pore diameter. The rate of calcination, which limits the rate at which CaO is available for reaction, is a function of sorbent type and particle diameter. The rate of sintering is a function of the concentration of CO_2 and H_2O in the gas phase and the surface area of the CaO grains. The required rate expressions were determined from the available fundamental literature, no adjustments were made to improve the agreement with the experimental results of this study. Product-layer diffusion coefficients were determined from the data of Borgwardt and Bruce (1986).

This comprehensive model is the result of an effort to account for the multitude of simultaneous processes that occur during dry sorbent injection in a combustion gas containing SO_2 . Fundamental data are inadequate in many instances to define the governing principles. Rather than ignore these areas of uncertainty, assumptions consistent with the structural model and the available literature data have been incorporated in the model.

ANALYSIS OF EXPERIMENTAL RESULTS

This section describes the extensive, high-temperature, time-resolved sulfation measurements obtained in a 30 kW isothermal dispersed-phase reactor. These investigations use commercial Linwood hydrate and carbonate sorbents derived from the same rock source.

The initial experimental studies were conducted with raw sorbents to characterize reactivity differences that would be expected in large-scale industrial applications. Figure 4 illustrates the time-resolved SO_2 capture data obtained for the Linwood carbonate and the hydrate. As observed by numerous other investigators (Bortz and Flament, 1985; Beittel et al., 1985; Overmoe et al., 1985), the ultimate SO_2 capture obtained with the hydrate significantly exceeds that obtained with the limestone. The time-resolved data in Figure 4 indicate that this difference is primarily due to a dramatic difference in initial sorbent

reactivity. After 0.15 s, the rates of reaction (the slopes) of the two curves are surprisingly similar.

The differences in reactivity exhibited by hydrate and carbonate sorbents are attributed to three factors. First, both sorbents must calcine to produce CaO, with its open, porous structure, prior to significant reaction with SO₂. For a given particle diameter, hydrates calcine much more rapidly than carbonates. Calculations using the activation model described above show that, under the conditions of Figure 4, the hydrate requires about 0.01 s to calcine while the carbonate requires about 0.3 s. Part of this difference in calcination time is due to a difference in particle size. Particle size is the second factor to which reactivity differences can be attributed. The mass mean diameters for the hydrate and carbonate are 2 and 25 μm , respectively. Larger CaO particles exhibit higher pore diffusion limitations which slow down sulfation. The third potentially important factor is a difference in the structure of the CaO produced from carbonate versus that produced from hydrate. However, as discussed below, this factor does not seem to affect sulfation rates.

The effect of particle size on capture and model predictions is shown in Figure 5 for the Linwood carbonate. The initial sulfation rate is strongly influenced by the mean particle size but the rate after 0.2 s is essentially independent of size. The apparent delay prior to the onset of sulfation exhibited by the largest carbonate particle is associated with pore diffusion and with the time required for significant calcination to occur. The model predictions shown in Figure 5 imply a stronger dependence on particle size than the 0.5 s capture data support. The model also underestimates short time reactivity. Time resolved sulfur capture data for the sized hydrates exhibit the same general dependence on particle size.

Figure 6 provides a direct comparison of the carbonate and hydrate data at a reaction time of 0.5 s. Figure 6 includes data obtained by Silcox et al. (1987) for the same two Linwood sorbents. These data represent exhaust measurements from a bench-scale furnace with a decaying thermal profile. Although these results are not directly comparable (isothermal vs. decaying thermal profile), they do indicate that at long times both facilities show a similar dependence on mean particle diameter. Figure 6 includes model predictions as the unbroken lines. Results are also presented for the unsized materials (solid symbols) and these data agree well with the sized results.

To clearly address the effects on sulfation of the delay in the availability of CaO sites due to calcination, capture data for hydrate and carbonate particles of comparable sizes (roughly 5 μm) are plotted in Figure 7, along with model predictions. These data suggest that for these small particles, the difference in calcination rate does not significantly affect extents of sulfation. The model predictions incorrectly show an initial sulfation advantage for the hydrate due to its more rapid calcination rate.

Figures 8 and 9 show the temperature dependence for SO₂ capture with Linwood carbonate and hydrate, respectively. The temperature data suggest an optimum isothermal sulfation temperature of

approximately 1400 K. Bortz and Flament (1985) and Newton and Kramlich (1987) suggest a higher optimum of 1450 K. The model predictions show an optimum of 1340 K. The model predicts the progressive flattening of the capture curve at longer reaction times with increasing temperature.

The effect of SO₂ concentration on capture for hydrate and carbonate is shown in Figure 10. Note that capture levels at low extents of sulfation (0.04 s) are relatively insensitive to increases in SO₂ partial pressure above 20 Pa. The capture levels at higher extents of sulfation (0.5 s) increase significantly with increasing partial pressure. There is an increase in reaction order with extent of sulfation. The model represents this variability in the SO₂ dependence by assuming that the initial sulfation rate, until a monolayer of CaSO₄ covers the individual grains, is limited only by gas-phase diffusion. Subsequent sulfation is limited by pore diffusion and product layer diffusion with an effective reaction order of 0.6.

CONCLUSIONS

The overlapping grain model which is used to represent the structure of CaO is consistent with visual observations obtained with SEM techniques. The sintering rate expression is based on the recent experimental data of Borgwardt (1988b) and it is used to estimate the change in center to center spacing for the overlapping grains. Extrapolation of surface area data yields an initial CaO surface area of 100 m²/g for small diameter CaCO₃ and Ca(OH)₂ particles calcined in a dispersed state. Porosity decreases in direct proportion to the change in surface area per particle volume.

The calcination rate equation is an empirically modified form of the shrinking-core model with a particle diameter dependence of $1/d_0^{0.6}$. The combined calcination and sintering model approximates high-temperature observations to within the accuracy of the data. The calcination and sintering models are designed as submodels for a comprehensive sulfation model.

The sulfation data confirm that the hydrated sorbents are superior to carbonate sorbents with respect to SO₂ capture. This difference is primarily due to the smaller size of the hydrate, which results in a dramatic difference in short time reactivity. The data also suggest that the large decrease in initial sulfur capture with increasing particle size appears to be primarily the result of initial pore diffusion effects because both raw and precalcined sorbents give similar capture levels. The sulfur capture data indicate that the overall sulfation rate of particles less than 5 μ m in mean diameter is not limited by calcination.

The optimum isothermal injection temperature is approximately 1400 K. The optimum results from the opposing tendencies of increased temperatures to increase sulfation rates while decreasing available surface area by increasing sintering rates.

The mathematical model shows reasonable agreement with the

observed capture trends and is reliable in predicting the relative changes in capture due to changes in SO₂ concentration. This agreement with the data illustrates that the product-layer diffusion model, with rate constants and diffusion coefficients based on the low temperature reactor data of Borgwardt and Bruce (1986), extrapolates to the high-temperature, short-time conditions experienced in dry sorbent injection. The injection of precalcines of known pore structure to obtain fundamental sulfation rate data by which the model might be calibrated, proved ineffective due to alteration of the CaO structure by the rapid heating that occurs upon injection.

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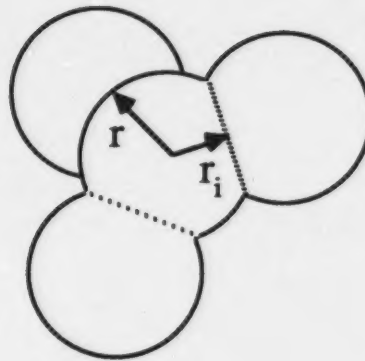


Figure 1. Illustration of the overlapping grain model.

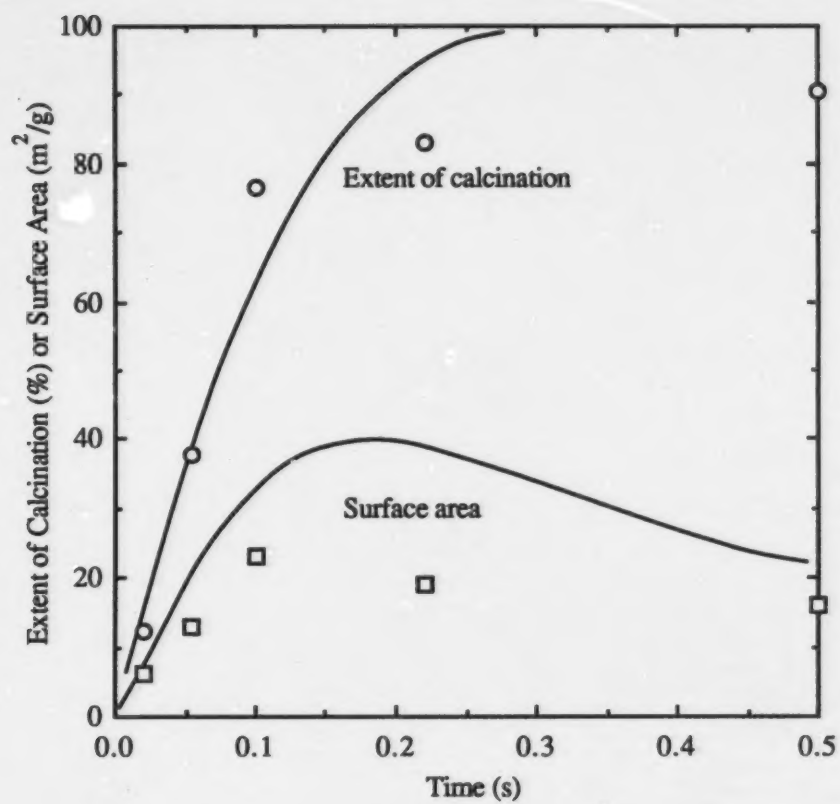


Figure 2. Model predictions for 13 μm Marianna limestone calcined at 1373 K in an isothermal flow reactor (Roman et al., 1986).

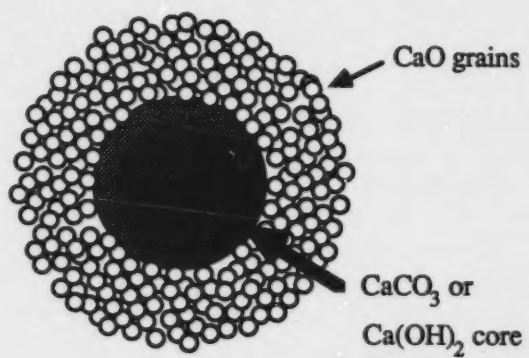


Figure 3. Illustration of the shrinking-core calcination model.

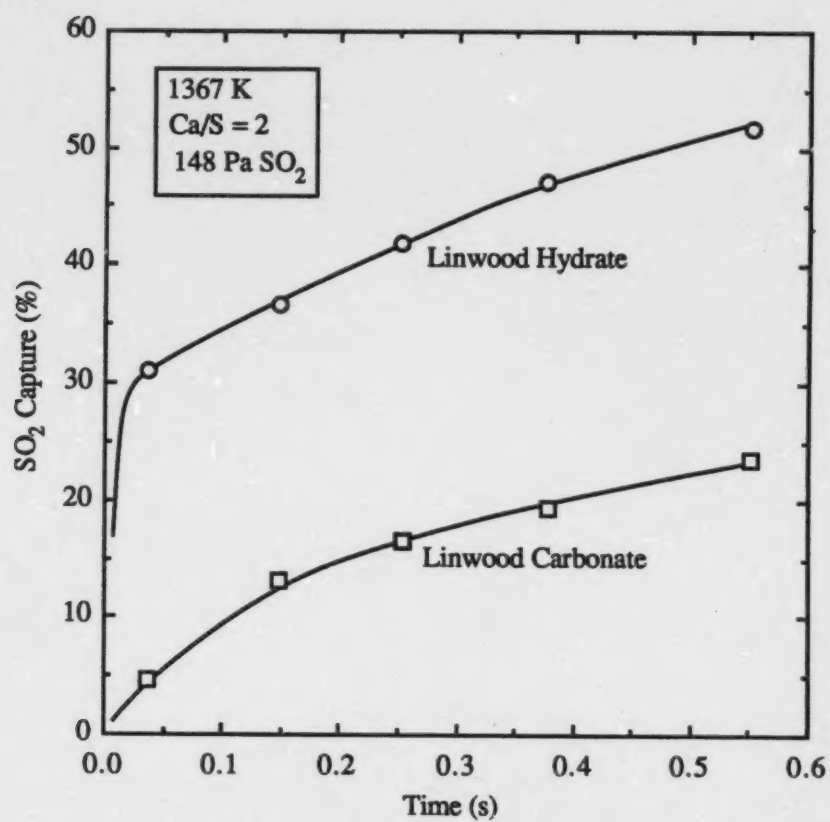


Figure 4. Sulfur-capture data for commercially available Linwood hydrate and carbonate.

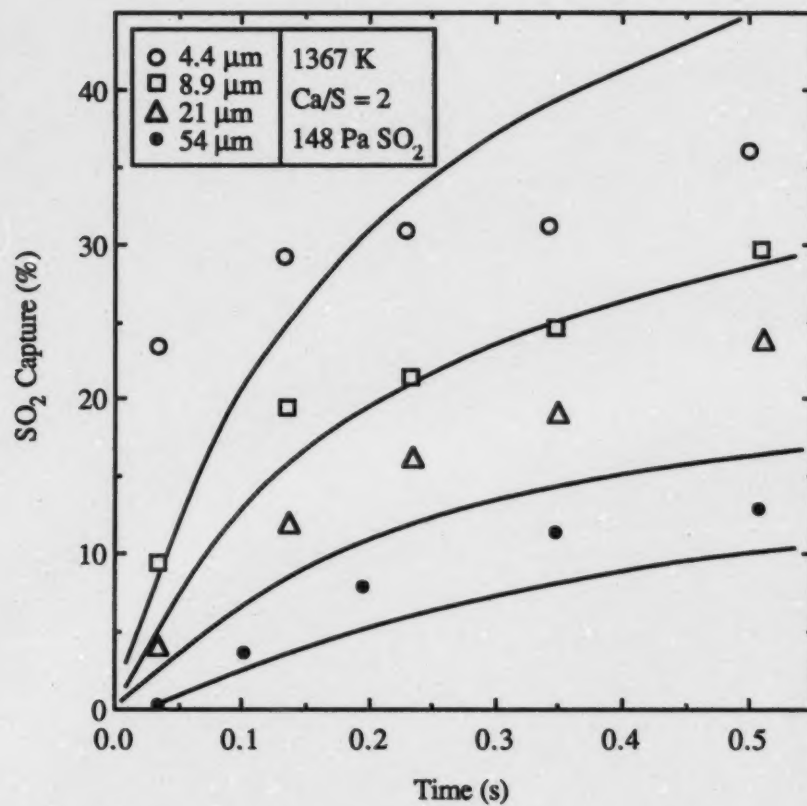


Figure 5. Influence of particle size on sulfation of Linwood carbonate: model predictions compared with experimental data.

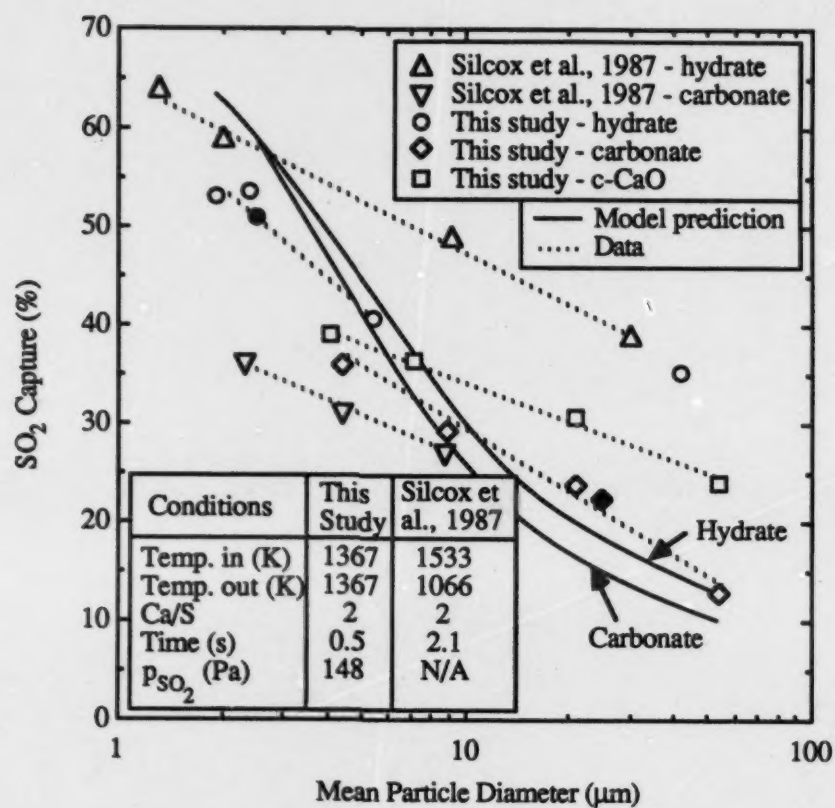


Figure 6. Sulfur capture as a function of particle diameter for Linwood hydrate and carbonate. Model predictions and experimental data from this study are compared with data from Silcox et al. (1987).

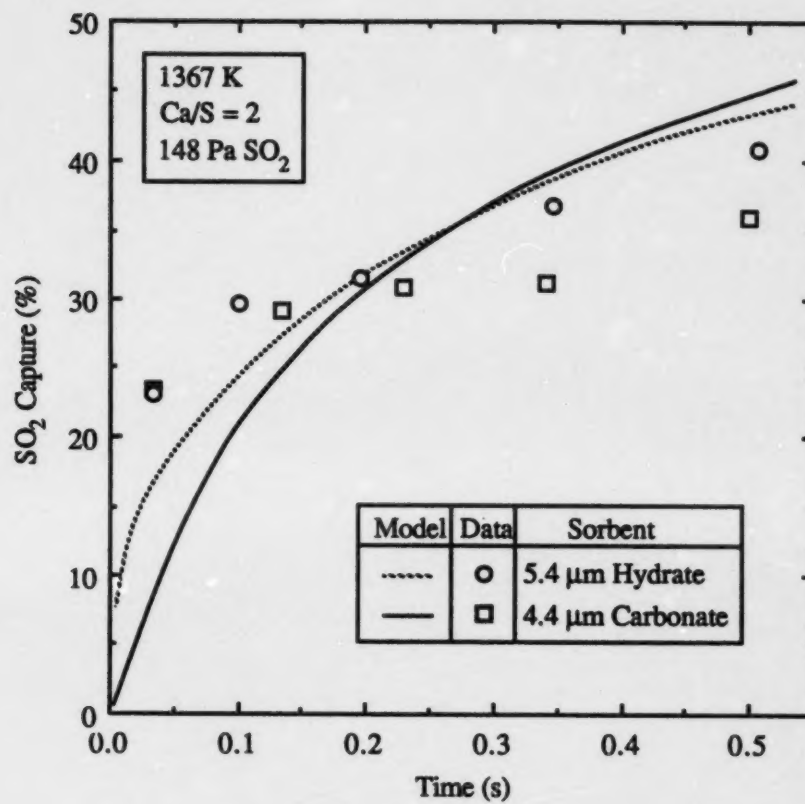


Figure 7. Sulfur capture for comparable size Linwood hydrate and carbonate particles: model predictions and experimental data.

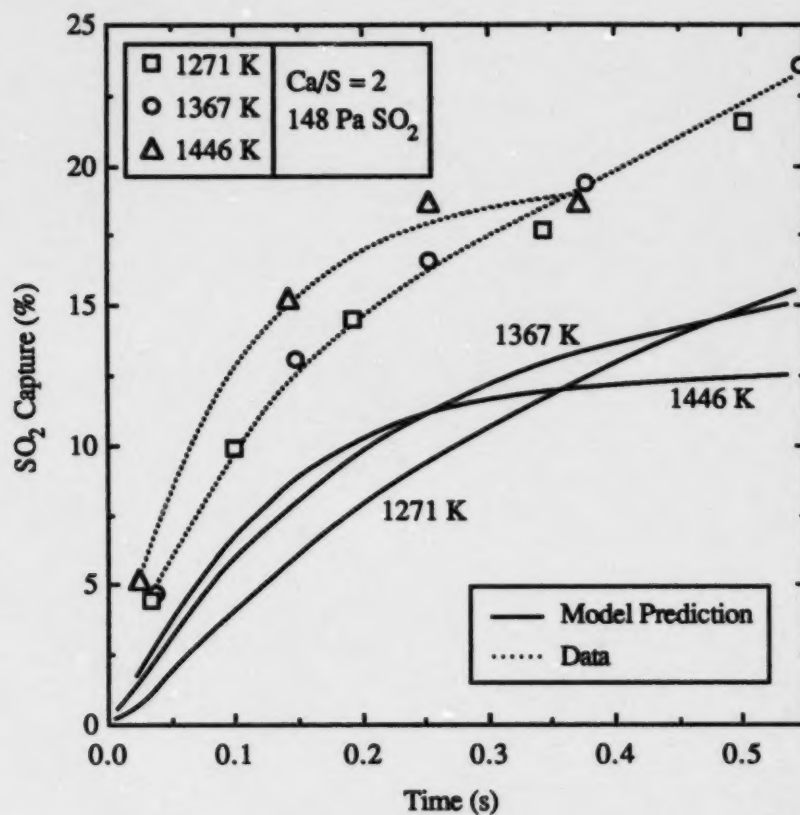


Figure 8. Sulfation of raw Linwood carbonate (25 $\mu\text{m mmd}$) as a function of temperature: model predictions compared with experimental data.

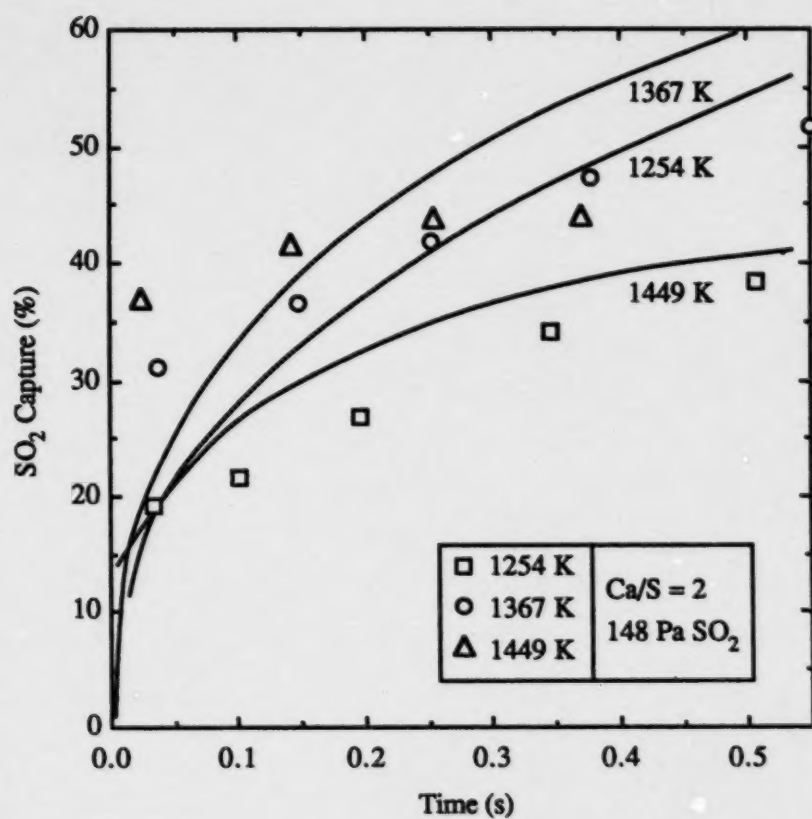


Figure 9. Temperature dependence for sulfation of raw Linwood hydrate (2.5 $\mu\text{m mmd}$): model predictions and experimental data.

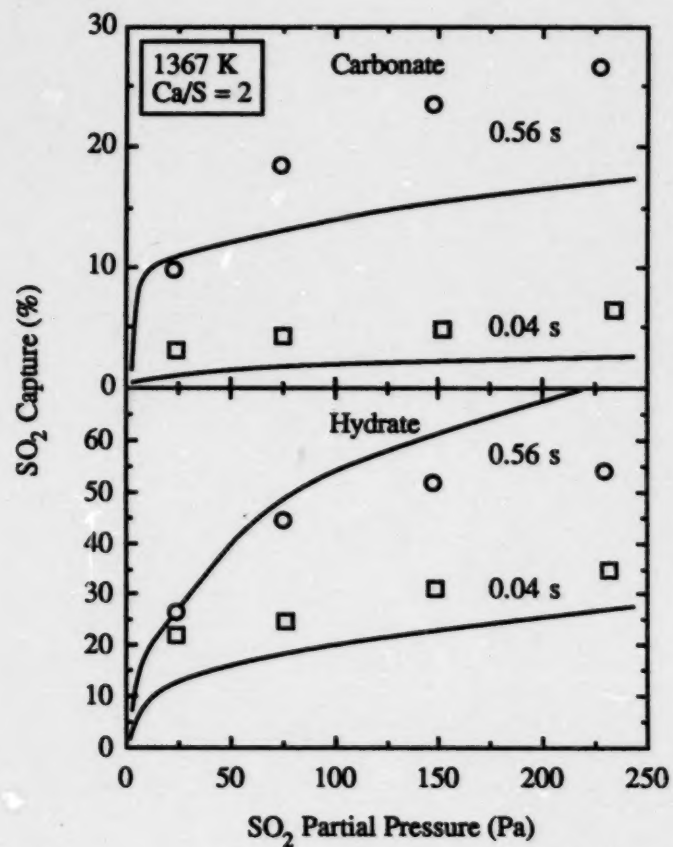


Figure 10. Influence of concentration on sulfur capture for raw Linwood carbonate ($25 \mu\text{m mmd}$) and hydrate ($2.5 \mu\text{m mmd}$): experimental data compared with model predictions.

DRY INJECTION - KINETIC STUDIES

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ABSTRACT

The reaction kinetics of fine limestone derived CaO with SO₂ was studied in a TGA equipment. The experiments were conducted at a low total pressure of 1 mbar. It was shown that the reaction can be well described by a two-stage process, the first is a fast surface reaction which is chemical reaction controlled and the second is a much slower reaction which is controlled by gas diffusion through product layer. A CaO-conversion of ~ 60 % was achieved during the first 2 seconds and at 1000 °C. The second stage fits with the shrinking core model.

The reaction was also studied in an entrained flow reactor. The reaction kinetic data calculated from the TGA experiments were used together with the entrained flow reactor model and a good agreement between model and experiments was obtained. A SO₂-reduction of ~ 70 % was measured at 1000 °C and a stoichiometric ratio of 1.5. Both theoretical analysis and experiments show that in order to get a high CaO-conversion in a dry injection process, the particle diameter should be less than 5 µm.

INTRODUCTION

Dry injection of limestone or lime into the combustion chamber in order to reduce the SO₂ emissions is a process which has been studied thoroughly during the last three decades. The literature contains very many papers addressing fundamental and technical problems of that process. In the early seventies the EPA evaluated a large number of studies carried out in pilot and laboratory scales (1). It was concluded that the limiting reaction step was within the particle and not in the gas phase. The limiting reaction in the particle can either be the chemical reaction between CaO and SO₂ or a diffusion process. The initial rate is always the largest but it is reduced by one or more of the following mechanisms:

1. Formation of a CaSO₄ product layer on the outer surface of the particles.
2. Formation of a CaSO₄ product layer on the pore surface (pore blocking).
3. Decreased reaction rate caused by loss of reactive surface area caused by crystal growth or sintering.

The initial reaction rate is mainly a function of the particle size and the pore structure of the calcined particle. Borgwardt (2) studied how the reaction rate is affected by particle size and pore structure. He found that differences in reactivity among different limestones could be explained by differences in the physical properties of calcined products. The pores formed during the calcining have a profound effect on the SO_2 reaction rate and the SO_2 uptake capacity. Small pores give high reaction rate but low capacity while large pores give low reaction rate but high capacity. In cases where the pores are larger than $0.1 \mu\text{m}$, the pore diffusion resistance can be neglected. A calcined limestone can, because of its pore volume, react with SO_2 to about 50 % without expanding. Calcined dolomite, however, has about twice as much pore volume as has the calcined limestone and can react to 100 % without expanding.

Weisweiler et al. (3) measured the sulfur distribution and determined pore size distribution in single grains with particle size $d_p = 300\text{--}900 \mu\text{m}$. A layer of CaSO_4 was found blocking pores $<100 \mu\text{m}$. In one case the conversion was 17 % but at the same time the pore volume was reduced by 80 %.

Schneider (4) studied the sulfation kinetics of calcined limestone with original particle size of $20\text{--}30 \mu\text{m}$. At about 20 % conversion of the solid, the reaction rate became very slow. The energy of activation for the sulfation reaction was determined to be 115 kJ/mol .

Dogu (5) determined the energy of activation for 1.5 cm particles and found it was 50.4 kJ/mol for initial reaction and 27.3 kJ/mol for the following reaction. According to the pore diffusion theory, the energy of activation for the surface reaction is cut in half when pore diffusion is the limiting step.

Borgwardt (6) studied the sulfation of several calcined limestones and found the activation energy for the initial reaction to be within $34\text{--}76 \text{ kJ/mol}$. A further finding was that at high CaO -conversion the reaction rate slowed down but the energy of activation did not change. In more recent studies, Borgwardt (7, 8, 9) studied the reaction rate of very small particles $\sim 1 \mu\text{m}$. The small particles were calcined in order to give different BET surfaces. The results were fitted to a shrinking core model with good results. The energy of activation was measured to 154 kJ/mol . Borgwardt suggests anion diffusion through the product layer as being the limiting step.

Cole et al. (10) studied the effect of particle size on SO_2 -removal. Limestone fractions in the range $0.1\text{--}10 \mu\text{m}$ were injected in an entrained bed reactor. Very low lime utilization was reported. A reason for this is probably agglomeration of the fine particles during and after injection.

Muzio (11) studied the reactivity of promoted slaked lime. A number of Na- and K-based promoters were investigated and an improved Ca utilization could be seen. An explanation given for this is that on the surfaces melts are formed which affect the reactions positively.

Slaughter (12) promoted Ca absorbents. The presence of Na in the CaO matrix reduces the particle size in some cases and almost spherical particles are formed, indicating that they have been formed through melts.

Borgwardt (13) also measured the sintering rate of CaO derived from limestone. He found that the sintering rate increased rapidly with temperature and also accelerated by the presence of impurities in the CaO . Based on Borgwardt's kinetic data it can be shown that it takes several minutes at 1000°C to get an appreciable reduction in the BET surface area. It can therefore be assumed that in

the dry injection process where the particle residence time is in the order of 1 second, the sintering process can be neglected.

In conclusion it can be said that particle size has a large effect on the absorbent utilization. Very few experiments have been carried out in which the particle size has been measured after the particles have been fed to the furnace. However, Borgwardt measured the reaction rate of small particles ($\sim 1 \mu\text{m}$) in a differential reactor and found high rates.

THEORY

GAS FILM DIFFUSION

The dry injection process can be modelled as a tubular reactor and if the gas film diffusion is assumed as the limiting step, the rate equation is shown below.

$$r_{\text{SO}_2} = -k_G \cdot (C_b - C_s)$$

$$C_s = 0, \quad C = C_b$$

The differential material balance for a tubular reactor can be written:

$$\frac{dC}{dt} = r_{\text{SO}_2} \cdot S$$

$$S = \frac{m \cdot 4 \cdot \pi \cdot r_p^2}{\rho_p \cdot \frac{4}{3} \cdot \pi \cdot r_p^3} = \frac{3 \cdot m}{\rho_p \cdot r_p}$$

$$C = C_0 \cdot (1 - x)$$

$$x = 1 - e^{-k_G \cdot \theta}$$

Example:

Basis: 1 m³ flue gas at 1000 °C

Gas conditions:

$$\text{SO}_2\text{-fraction} = 500 \text{ ppm}$$

$$C_0 = [\text{ppm SO}_2] \cdot 10^{-6} \cdot 273 / 22.4 / 1273$$

$$s = 2$$

$$D_{\text{SO}_2} (1000 \text{ °C}) = 2 \cdot 10^{-4}$$

$$\rho_p = 2700$$

$$M = 100$$

$$m = s \cdot C_0 \cdot M = 9.6 \cdot 10^{-4}$$

$$\theta = 1$$

Mass transfer condition:

$$Sh = 2 = \frac{k_G \cdot d_p}{D_{\text{SO}_2}}$$

$$k_G = \frac{D_{\text{SO}_2}}{r_p}$$

Rate constant:

$$k_v = k_g \cdot S = \frac{3 \cdot m \cdot D_{SO_2}}{r_p^2 \cdot \rho_p} = \frac{213 \cdot 10^{-12}}{r_p^2}$$

The results from calculation are as follows:

particle radius, μm	conversion, %
10	88
20	41
30	21
40	12
50	8
60	6
70	4
80	3

It is obvious from the results, that the particle size determines to a large extent the efficiency of the process. Particles with radii above 40 μm contribute only slightly to the SO_2 -conversion. In order to eliminate most of the gas phase resistance the particle radii should be well below 10 μm .

PRODUCT LAYER DIFFUSION

After a short initial period with a high reaction rate, a product layer of CaSO_4 is formed and the rate is drastically reduced. The particles on the Pt-wires of the sample basket form a thin continuous layer. Plane symmetry can be assumed as the Pt-wires have a diameter of 200 μm and the layer thickness is in the order of 1 μm .

According to Levenspiel (14) the shrinking core model assuming plane symmetry and diffusion through the formed product layer is:

$$\frac{dy}{dt} = \frac{D_{\text{eff}} \cdot C_0 \cdot M}{y \cdot \rho_p \cdot L^2}$$

$$M = 56$$

$$\rho_p = 3300$$

In integrated form the equation can be written:

$$y^2 = \frac{2 \cdot D_{\text{eff}} \cdot C_0 \cdot M \cdot t}{\rho_p \cdot L^2}$$

The layer thickness distribution curve from the dissolution experiment is approximated with ten layer thicknesses. For a chosen time the conversion of the ten thicknesses are calculated and multiplied by their corresponding weight factors and added together. The obtained conversion is compared with the corresponding conversion read from the TGA-curve. D_{eff} is varied until the best fit is obtained. The conversion during the initial period is used as the base line for the shrinking core model.

SURFACE REACTION

In the TGA-reactor the SO_2 concentration is kept constant and a differential material balance for the CaO -conversion can be written:

$$\frac{dy}{dt} = k_v \cdot (1 - y) \cdot C_0$$

In an entrained flow reactor both the SO₂ concentration and the CaO concentration vary with time. A differential material balance for the CaO-conversion can for this case be written:

$$\frac{dy}{dt} = k_v \cdot C_0 \cdot (1 - x) \cdot (1 - y)$$

$$x = s \cdot y$$

$$\frac{dy}{dt} = k_v \cdot C_0 \cdot (1 - s \cdot y) \cdot (1 - y)$$

$$y = \frac{e^a - 1}{s \cdot e^a - 1} \quad s \neq 1$$

$$a = k_v \cdot C_0 \cdot (s - 1) \cdot \theta$$

EXPERIMENTAL

TGA-MEASUREMENTS

The reaction between CaO and SO₂ was studied in a TGA instrument on two limestone qualities (see Table 1). It has been shown that in order to eliminate the gas phase resistance the particle size should be well below 10 μm. Normally in a TGA instrument the sample basket acts as a single large particle surrounded by a gas film which limits the reaction between CaO and SO₂ causing extremely low reaction rates to be measured. In order to eliminate the gas phase resistance in this study an inert free reactant gas of SO₂ and O₂ was used. The reactant gas was introduced in the TGA instrument after the system had been completely evacuated. The total pressure in a standard experiment was 1 mbar. The partial pressure of SO₂ was adjusted to 0.67 mbar, the rest up to 1 mbar being O₂. In a flue gas with a SO₂ partial pressure of 0.67 mbar, the SO₂ fraction is about 670 ppm.

The TGA instrument used in the study was a Cahn-2000 with a sample basket made of a fine Pt-net. The basket was hanging in a quartz reactor which was surrounded by a furnace which could bring the temperature up to 1250 °C. The reactant gas could be fed to the system via two inlet ports, one of them connected to the balance casing and one to the quartz reactor, as shown in Figure 1.

At the sample preparation, the basket was dipped in a slurry containing 10-15% limestone whereby about 5 mg of limestone adhered to the basket. The basket was dried in IR-light and the amount of limestone adhered was determined by weighing.

The sample basket was heated to 400 °C in N₂ atmosphere in the quartz reactor and was kept at this temperature for a couple of minutes for dewatering whereafter the sample was heated at 200 °C / min to 900 °C where the calcining took place. After completion of the calcining step, the TGA equipment was evacuated and N₂ was fed to the system in such an amount that the pressure was kept at 1 mbar. The temperature was adjusted at the same time to the sulfation temperature.

The gas feed through the quartz reactor port was started and adjusted to a value causing the basket to lose 3 mg in weight. The gas feed dose to the basket was necessary in order to avoid gas diffusion as being the limiting step.

At time zero, the reactant gas feed was started. About 2 min had elapsed from the finishing of the calcining step. The reaction rate was very fast during the first seconds, but after 10 seconds the rate leveled off. Every experiment was followed by a blank experiment in which everything was identical except that the basket did not have any limestone material adhering to it. The blank curve was subtracted from the corresponding experimental curve.

The reaction rate during the first seconds was very fast and caused the balance to oscillate. The same type of oscillation but in the opposite direction could be noticed when quick calcining was performed in vacuum. Normally the calcining took place in a N₂ atmosphere. The calcining based on the TGA curve was always compared with the theoretical calcining which could be calculated from the amount of limestone adhering to the basket. Only those experiments showing a good agreement $\pm 5\%$ between the two values were accepted.

DETERMINATION OF LAYER THICKNESS ON THE Pt-BASKET

The sample basket is prepared in the same way as for the TGA measurements. The thickness of the limestone film is determined by dissolution experiments in a pH-stat. The basket with adhering sample is immersed in a stirred solution kept at pH = 3. At the time the immersion takes place 0.01 M HCl has to be fed to the solution in order to keep the pH at 3. The feed rate of the HCl solution is proportional to the limestone dissolution from the basket.

Flat symmetry can be assumed because of the very thin limestone layer on the wires of the basket. The limestone dissolution is governed by mass transfer of hydrogen ions through the liquid boundary layers surrounding the wires on the basket.

The dissolution rate:

$$\frac{dz}{dt} = \frac{A \cdot M}{L \cdot \rho_p}$$

$$A = 3 \cdot 10^{-7}$$

$$\rho_p = 2700$$

$$M = 100$$

According to Wallin and Bjerle (15) the limestone dissolution rate from a rotating cylinder at pH = 3 and a rpm of 800 is equal to the A-value given above. In integrated form the dissolution equation can be written,

$$z = \frac{1.1 \cdot 10^{-8} \cdot t}{L}$$

The dissolution equation can be used as a link between the pH-stat produced dissolution curve and the layer thickness distribution curve.

A distribution curve is guessed and from this curve about ten layer thicknesses are chosen. Also some time points are chosen in such a way that they can be evenly spread out along the dissolution curve. At every chosen time point the dissolution value z for every layer thickness is calculated and summed up. The value obtained is compared with the corresponding experimental dissolution value. Through trial and error the distribution curve was changed until a satisfying agreement between the distribution curve and dissolution curve was reached.

Thiele modulus describes the reactivity within a solid particle. The characteristic length in the module is the particle volume divided by the particle

boundary surface. For a spherical particle the length is $d_p/6$ and for the layer in this case it is the layer thickness L . A Thiele module less than one means that the reaction takes place without pore diffusion restriction.

ENTRAINED FLOW REACTOR TESTS

The reaction between sulfur dioxide and limestone was also investigated in an entrained flow reactor. Figure 2 is a schematic diagram of the equipment. The entrained flow reactor consists of two tubular furnaces in series. With these furnaces the temperature in the tube can be varied between 100 and 1500 °C. The limestone tested is Forsby Stone from the same slurry as was used in the TGA experiments. The slurry was dried and mixed into an air stream to which sulfur dioxide was also added. The concentration of SO_2 was kept at 1000 ppm in the experiments. The residence time in the hot zone could easily be varied by adjusting the gas flow. Normally the gas flow was so adjusted that two seconds residence time, which corresponds to the residence time in a commercial unit, was achieved.

The waste material was collected on glass wool at 450 °C. At that temperature the reactivity of limestone is very low. To be able to determine the CaO-conversion exactly the waste material was analyzed both on calcium and sulfur. The gas from the entrained flow reactor was analysed with an UV- SO_2 -gas analyzer.

The experiment was started by heating the furnaces to the desired temperature. The gas flow was then turned on and the SO_2 concentration was measured. When constant SO_2 concentration was obtained the limestone was mixed into the gas stream and the SO_2 reduction was measured. After 20 minutes the limestone addition was turned off and the SO_2 concentration went back to its original level.

RESULTS

TGA-MEASUREMENTS

The weight increase versus time for SO_2 reacting with CaO was continuously measured by the thermo-balance and registered by the recorder. Figures 3 and 4 show the weight increase versus time in a set of normal experiments conducted at different temperatures. The curves show a very fast initial reaction during the first two seconds. In some experiments it was so fast that an oscillation at the beginning superposed on the weight curve. A slower weight increase followed. It is quite reasonable to get the CaO-conversion at the first 2 seconds by taking the intersection of the extrapolated flat curve and the initial steep curve. Figure 5 shows CaO-conversion versus time for the two limestones at 1000 °C with the oscillation peak eliminated. The CaO utilized during the first 2 s is 40 - 60% and 75 - 85% after 15 min.

The temperature dependence of the reaction can also be seen in Figure 3 for Forsby Stone and in Figure 4 for Ignaberga Stone. It is shown from the figures that the reaction rate increases with increasing temperature up to 1050 °C. After that it decreases and above 1200 °C no reaction will take place. The equilibrium partial pressure of SO_2 over $CaSO_4$ is given by the formula.

$$p_{SO_2} = 4.72 \cdot 10^{11} \cdot \exp(-37286 / T)$$

According to the formula there should not be any reaction at 1100 °C. However the experiments still show a high CaO-conversion. The explanation can be that the equilibrium is not achieved or the sample temperature is not that measured.

Surface reaction versus temperature can be seen in Figure 6. The best reaction is obtained with Forsby Stone at 1000-1100 °C. At that temperature 58% CaO-conversion is reached after 2s and 85% after 15 minutes.

Experiments were done at different pressures but still with a stoichiometric ratio. The results are shown in Figure 7, which shows that the surface reaction is faster with increasing partial pressure of SO_2 but the final conversion is only slightly affected.

Experiments were also done to see if the CaO reactivity changes when it is exposed to high temperatures. The sintering time was varied as well as the temperature. Figure 8 shows the CaO -conversion after 0.5, 1 and 2 min of sulfation at 1000°C versus sintering time at the same temperature. The results show that the rate of sulfation decreases with increased sintering time and that the decrease is faster between 2 and 5 minutes of sintering time than that between 5 and 20 minutes. Figure 9 shows the effect of different sintering temperatures on sulfation at 1000°C and 5 min sintering time. The figure also shows that the CaO -conversion decreases with increased sintering temperature.

The TGA experiments were done on two different limestone slurries but almost the same particle size distribution, the same layer thickness on the Pt-basket and the same initial BET surface. In spite of that they reacted at different rates. From figure 6 it can be seen how the surface reaction varies between the two limestones at different temperatures. The difference in reactivity of the two limestones also extends into the slow reaction period, as shown in Figure 5.

ENTRAINED FLOW REACTOR TESTS

The results from the experiments in the entrained flow reactor with Forsby Stone show that a ~ 70 % SO_2 -reduction, or a CaO -conversion of 50 % occurs at 1000°C , two seconds residence time and a Ca/S molar ratio between 1 and 1.5. The results are shown in Figure 10. The particle size distribution at the inlet of the entrained flow reactor measured by the Malvern Laser Diffraction Particle Sizer is shown in Figure 11.

DETERMINATION OF LAYER THICKNESS ON THE Pt-BASKET

The layer thickness distribution curves of the limestone on the Pt-basket were obtained from the corresponding experimental dissolution results by trial and error, and are shown in Figures 12 and 13. It is shown that only a thin layer of limestone adhered to the wires, and this was further confirmed by the scanning-electron-microscopy (SEM). The characteristic length distribution curves of the particles in the original slurries, which were calculated directly from the particle size distribution curves measured by sedigraph, were also given in the figures as a comparison. It shows that the original limestone particles give an order of magnitude smaller Thiele modulus than the limestone layer on the basket. This implies that if the agglomeration of the fine particles could be fully avoided in a real injection process, a high CaO -conversion would be expected.

BET SURFACE MEASUREMENTS

The surface of the limestone on the Pt-basket was measured both before and after calcination by BET method using nitrogen adsorption at -195°C . The calcination was performed in the BET equipment under vacuum at 1000°C .

The limestone surfaces were measured and found to be $13\text{--}15\text{ m}^2/\text{g}$, see Figure 14. During calcining the surfaces increased to $90\text{--}110\text{ m}^2/\text{g}$. If the calcined particles were exposed to high temperatures, sintering took place and the surface areas were reduced. After 5 minutes the BET surfaces were between 10 and $42\text{ m}^2/\text{g}$ and after 60 minutes approximately $10\text{ m}^2/\text{g}$. The rate of sintering varied for the two different limestones, and the sintering rate during the first seconds could not be determined with high accuracy.

DISCUSSION

SURFACE REACTION

The surface reaction took place during the first two seconds of the experiment and because of the very fast weight change the balance gave an oscillatory response which could not be completely countered by changing the damping factor. Only for those TGA experiments at 1000 °C which did not show an oscillatory behavior, could the kinetic constant be evaluated and for Forsby Stone it was found to be:

$$k_v = 6.7 \cdot 10^4$$

The rate constant was used to calculate the conversion in an entrained flow reactor at 1000 °C, 2 seconds residence time and 1000 ppm SO₂ in the inlet gas. In Figure 10 the calculated values are compared with experimental results from an entrained flow reactor and very good agreement between model and experiments has been achieved.

PORE DIFFUSION

By using the found rate constant and estimating the diffusion coefficient for SO₂ within the particles the particle size which does not give any pore diffusion resistance can be calculated. The effectiveness factor E for the reaction taking place in the pores is,

$$E = \frac{\tanh \gamma}{\gamma}$$

When $E \rightarrow 1$ the reaction takes place uniformly in the pores of the particles.

$$\gamma = \frac{r_p}{3} \sqrt{\frac{k_v \cdot p_p}{D_{eff} \cdot H}}$$

p_p / H = molar concentration of CaO in the particle

It can be assumed that the density of the calcined particles is reduced by the molar ratio 56/100 where 56 is the molar weight of CaO and 100 the molar weight of CaCO₃. Therefore the particle density is

$$\rho_p = 2700 \cdot 56 / 100 = 1512$$

For a small pore radius D_{eff} is equal to the Knudsen diffusion coefficient D_k

$$D_k = 98 \cdot r_{av} \cdot \sqrt{\frac{1}{H}}$$

$$H = 64$$

The average pore radius can be calculated from the BET surface S_m and is,

$$r_{av} = 2 \cdot \frac{V_p}{S_m}$$

$$V_p = \frac{1}{2700} \cdot \frac{100}{56} - \frac{1}{3300} = 3.58 \cdot 10^{-4}$$

The following results can be obtained by calculation:

$r_p, \mu\text{m}$	E
1.5	0.94
2.0	0.9
3	0.8
5	0.6
10	0.32

$$S_m = 110 \cdot 10^3$$

$$k_v = 6.7 \cdot 10^4$$

The calculation clearly shows that in order to utilize the pore structure of the particles the particle radius should be in the order of 2-3 μm . However when the reaction is proceeding the pores are filled up with reaction products and the pore radius is reduced. Therefore in order to fully utilize the particles they probably should have a radius well below 2 μm .

PRODUCT LAYER DIFFUSION

After the fast surface reaction a slower reaction follows during which a layer of CaSO_4 is formed around the CaO core. The model which best fits with the weight curves from the TGA experiments during this slow reaction is the shrinking core model with the assumption of plane symmetry and first order reaction with respect to SO_2 . The fit of the model to the experiments at different temperatures is shown in Figures 15 and 16, and is obviously rather good.

The diffusion coefficients at 1000 °C for the different limestones are between $10 \cdot 10^{-10}$ and $12 \cdot 10^{-10} \text{ m}^2/\text{s}$. In Figure 17 the effect of temperature on the diffusion coefficients is shown.

NOMENCLATURE

A	Limestone dissolution rate	$\text{kmol}/\text{m}^2/\text{s}$
C	SO_2 concentration	kmol/m^3
C_0	SO_2 inlet concentration	kmol/m^3
C_b	SO_2 bulk concentration	kmol/m^3
C_s	SO_2 surface concentration	kmol/m^3
D_{SO_2}	Diffusion coefficient, gas phase	m^2/s
D_{eff}	Diffusion coefficient, solid phase	m^2/s
D_k	Knudsen diffusion coefficient	m^2/s
d_p	Particle diameter	m
E	Effectiveness factor	
k_g	Mass transfer coefficient	m/s
k_v	Rate constant	$1/\text{s}$
k_v	Rate constant	$1/\text{s} \cdot \text{m}^3/\text{kmol}$
L	Layer thickness	m
m	CaCO_3 concentration in gas	kg/kmol
p_{SO_2}	SO_2 partial pressure	mbar
r_p	Particle radius	m
r_{SO_2}	SO_2 reaction rate	$\text{kmol}/\text{m}^2/\text{s}$
r_{av}	Average pore radius	m
s	Stoichiometry (CaO / SO_2)	
S	Reactive surface / reactor volume	m^2/m^3
S_m	Reactive surface / particle mass	m^2/kg
Sh	Sherwood number	
t	Time	s
T	Temperature	K
V_p	Pore volume	m^3/kg

x	SO ₂ -conversion	
y	CaO-conversion	
z	CaCO ₃ -conversion	
ρ_p	Particle density	kg/m ³
θ	Residence time	s
γ	Thiele modulus	

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ACKNOWLEDGMENT

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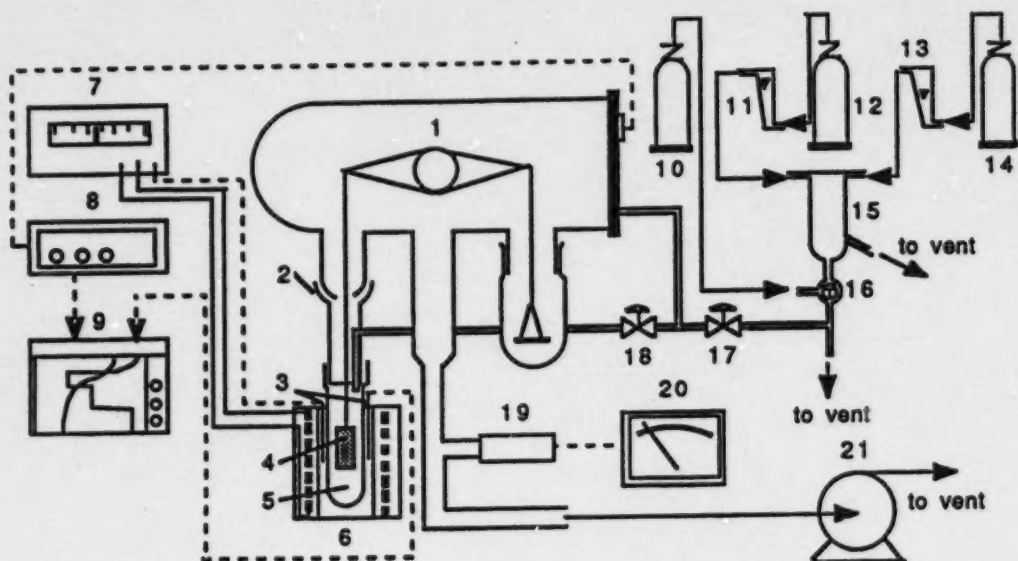


Figure 1. A schematic diagram of the TGA equipment

- 1- CAHN 2000 electrobalance 2- hemispherical connector 3- thermocouples
 4- sample holder 5- quartz reactor 6- electric furnace 7- temperature controller
 8- CAHN control unit 9- strip recorder 10- N₂ 11- rotameter for SO₂ 12- SO₂
 13- rotameter for O₂ 14- O₂ 15- reactant gas mixer 16- three-way valve
 17- valve for upper inlet 18- valve for reactor inlet 19- pressure transducer
 20- pressure meter 21- vacuum pump

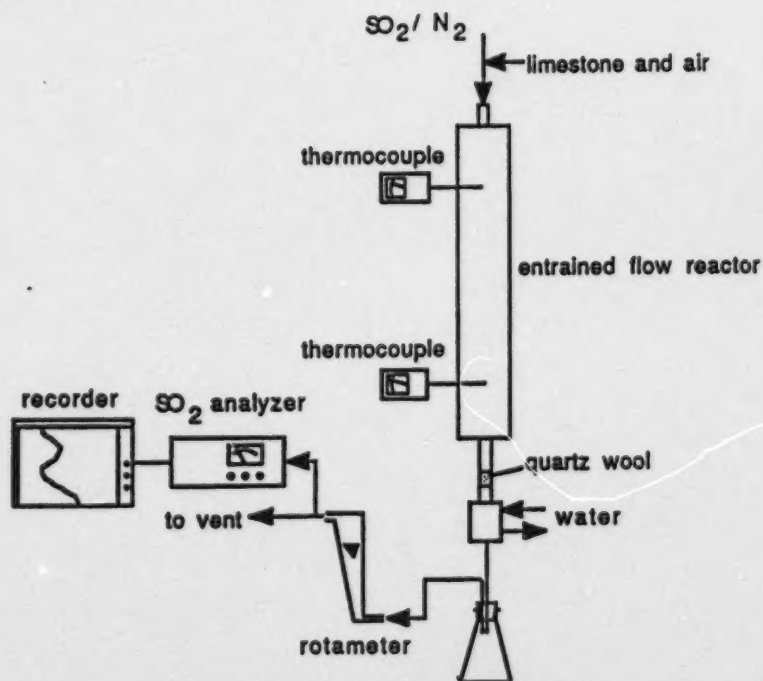


Figure 2. A schematic diagram of the entrained flow reactor

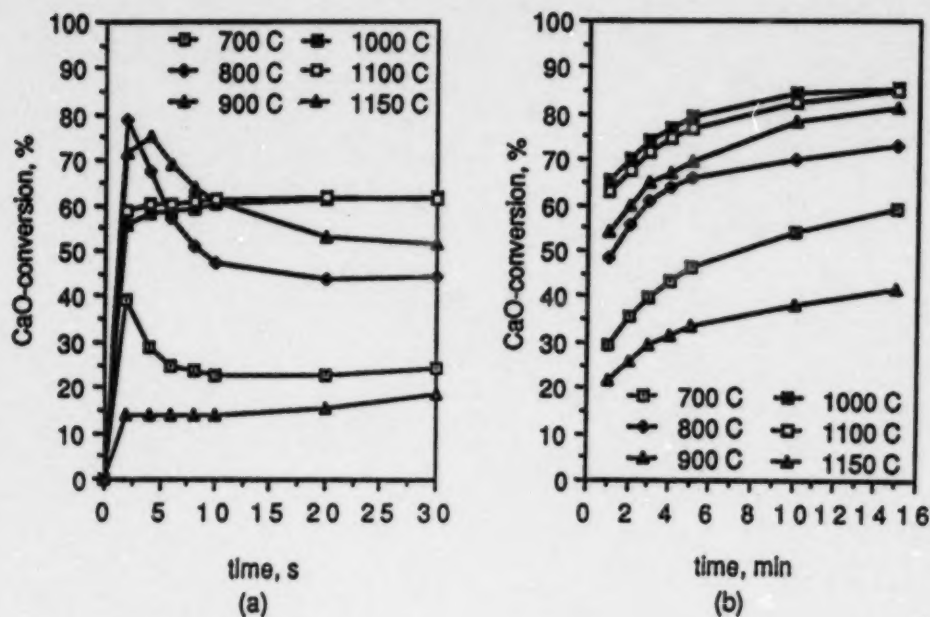


Figure 3. TGA curves obtained from Forsby (1 mbar)
(a) 0-30 s, (b) 1-15 min

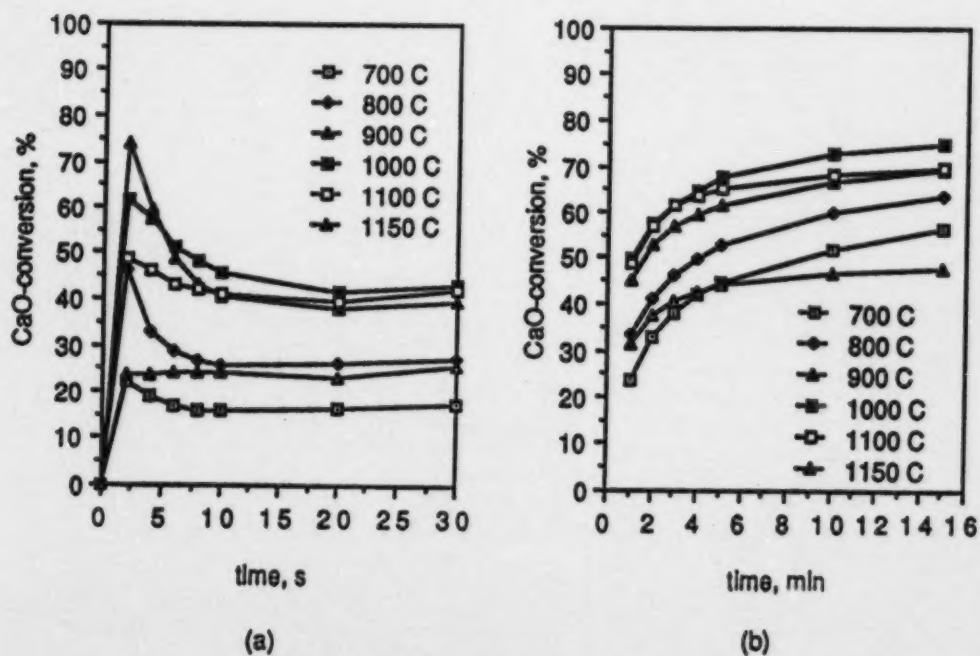


Figure 4. TGA curves obtained from Ignaberga (1mbar)
(a) 0-30 s, (b) 1-15 min

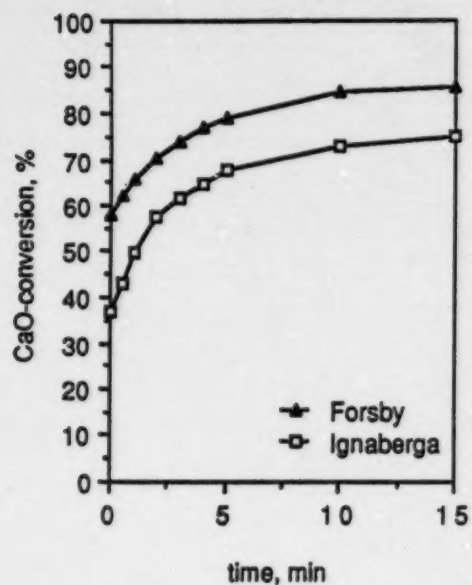


Figure 5. CaO-conversion at 1000 °C versus sulfation time for two different limestone qualities

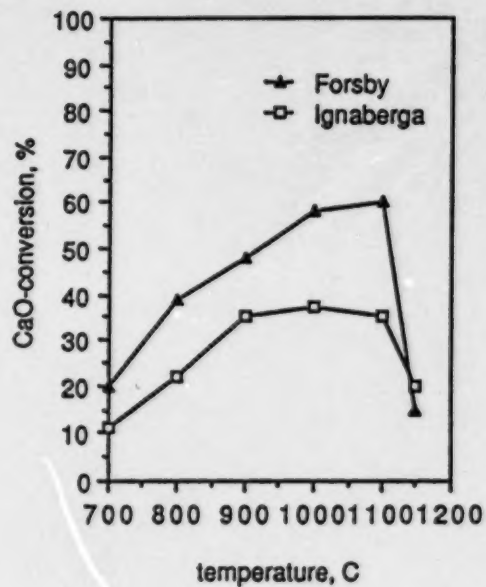


Figure 6. CaO - conversion versus temperature after 2 seconds of sulfation

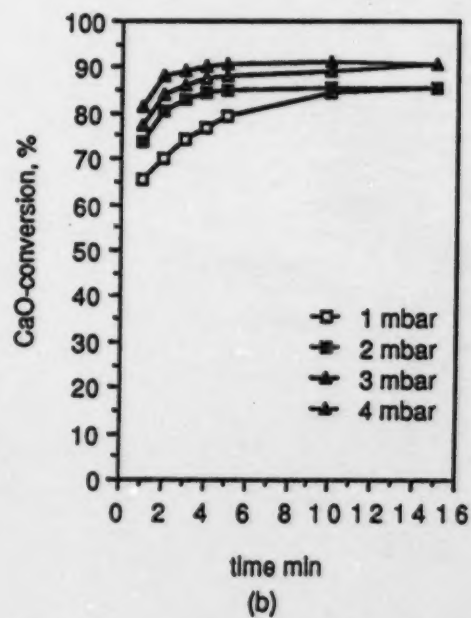
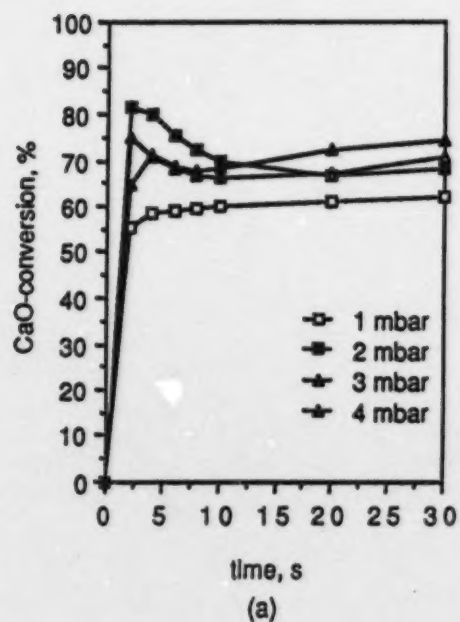


Figure 7. TGA curves obtained from Forsby at 1000 °C and different pressures
(a) 0-30 s, (b) 1-15 min

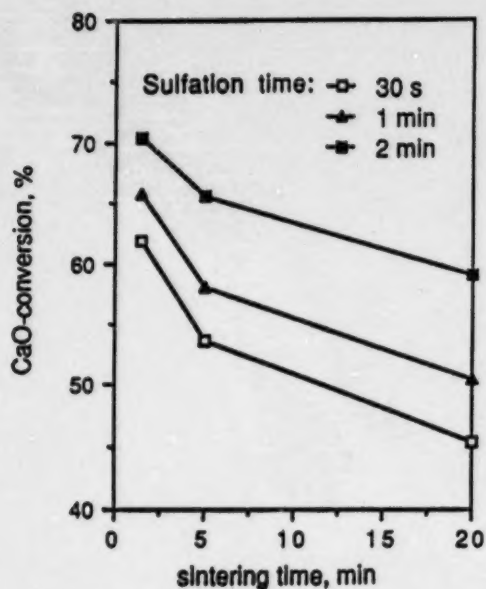


Figure 8. CaO - conversion versus sintering time at 1000 °C
Limestone: Forsby

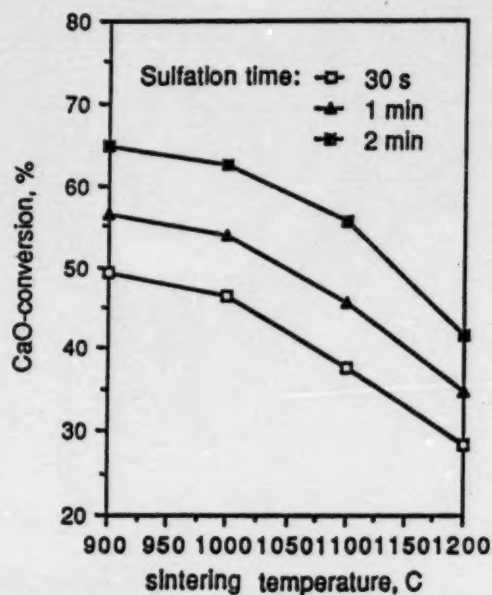


Figure 9. CaO-conversion versus sintering temperature
Limestone: Forsby
Calcining temperature: 900 °C
Sintering time: 5 min

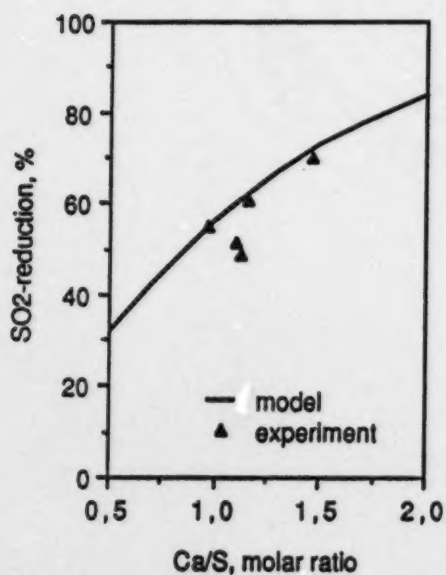


Figure 10. Results from entrained flow reactor compared with the model
Temperature: 1000 °C
Residence time: 2s

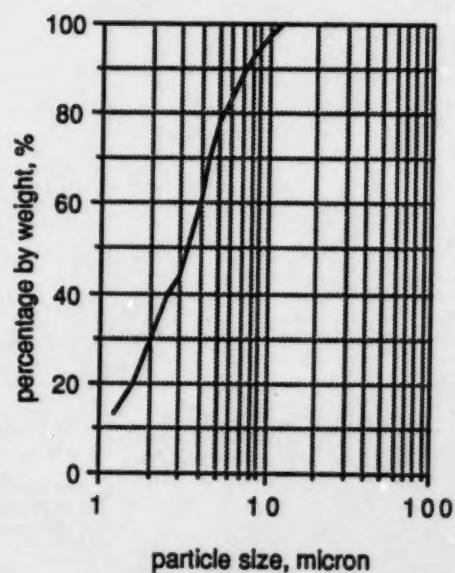


Figure 11. The particle size distribution at the inlet of the entrained flow reactor

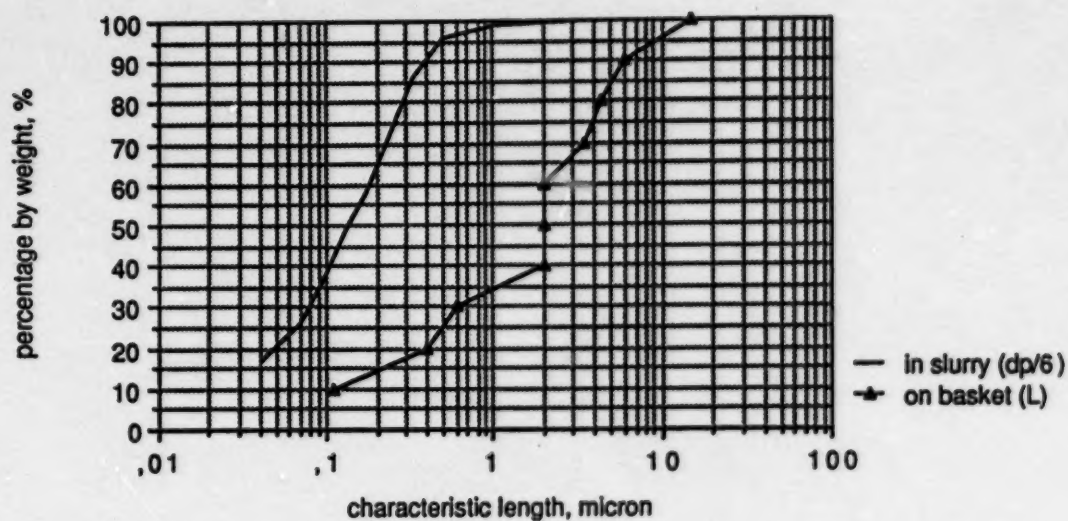


Figure 12. Characteristic length and layer thickness distribution measured from Forsby

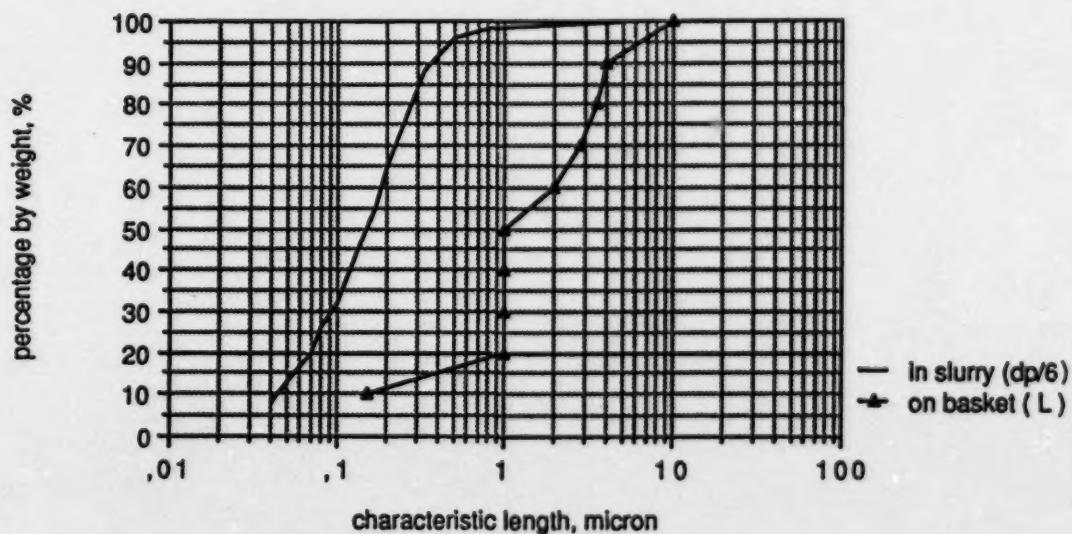


Figure 13. Characteristic length and layer thickness distribution measured from Ignaberga

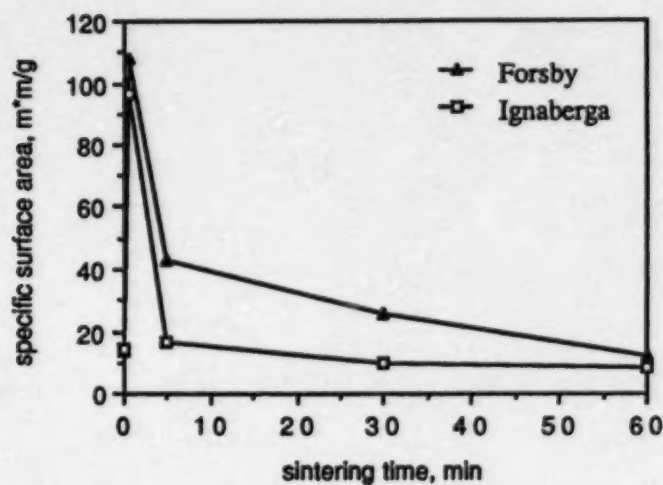


Figure 14. BET surface area versus sintering time
Temperature: 1000 °C
The data at time zero refer to the uncalcined limestone surface area

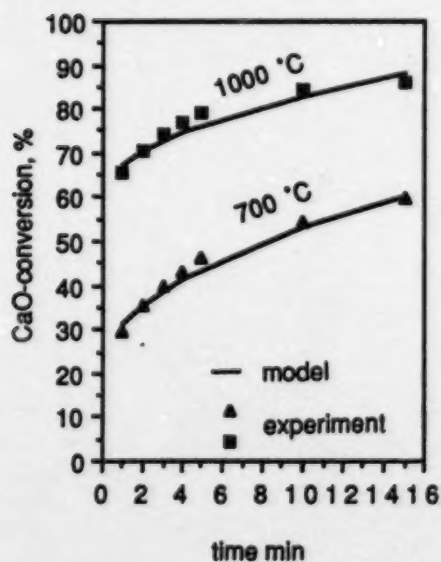


Figure 15. Results from TGA experiments compared with the shrinking core model
Limestone: Forsby

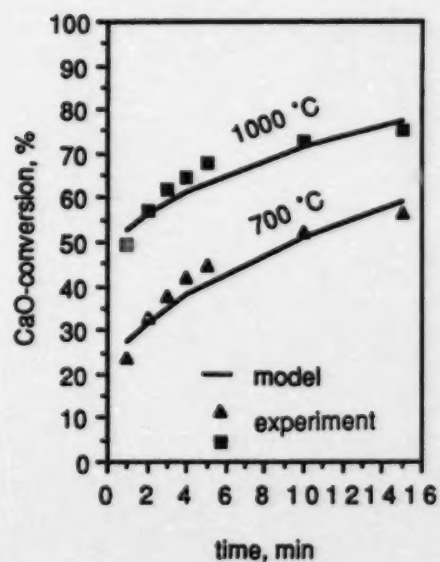


Figure 16. Results from TGA experiments compared with the shrinking core model
Limestone: Ignaberga

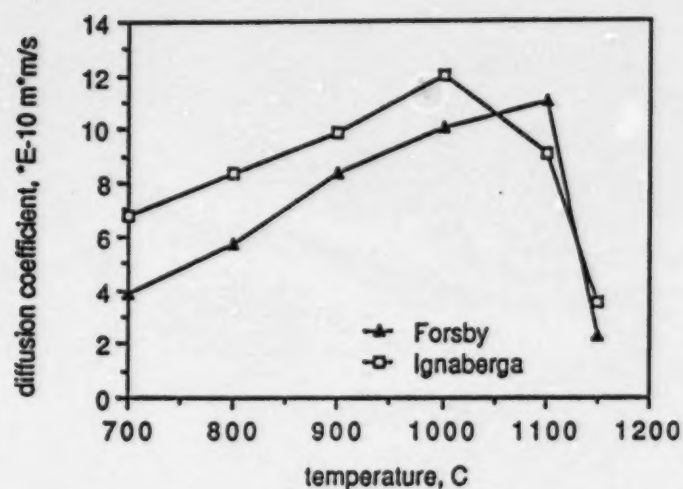


Figure 17. Diffusion coefficients at different temperatures calculated from the model (1 mbar)

Table 1. Two limestone qualities used in this study

	Forsby	Ignaberga
type of mineral	archeantime	cretaceous
constituents:		
CaCO ₃	95.6	82.8
SiO ₂	0.26	12.39
Al ₂ O ₃	0.3	0.89
Fe ₂ O ₃	0.23	0.66
MgO/Mg(OH) ₂	2.11	0.84
K ₂ SO ₄ ,Na ₂ SO ₄	0.24	0.56
BET surface (m ² /g)	13.6	14.1
BET surface right after calcining (m ² /g)	108	96.3
particle size, micron	86.5% < 2 58% < 1	88.2% < 2 55% < 1

LABORATORY TESTS ON FLUE GAS DESULFURIZATION BY DRY LIMESTONE INJECTION

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ABSTRACT

The reaction kinetics of the dry limestone injection process was studied at temperatures between 800 and 1200 °C and exposure times between 3 and 12 sec. Sieve fractions of a calcitic natural limestone, ranging from <5 to 90 µm, were treated at different SO₂- (500-5000 ppm), O₂- (2-8 %) and CO₂- (6-14 %) concentrations in the flue gas.

By calcination of the limestone a fine-porous structure develops within the solid reactant (CaO), which rapidly decreases by sintering. These sintering effects, which are dependent on temperature and CO₂-concentration, together with the formation of a solid product layer at the pore walls are the main causes of the complex behaviour of the reaction.

By temperature and particle-size effects on the conversion it is shown that one can distinguish three temperature ranges with different prevailing mechanisms of reaction, namely a region with chemical control at temperatures below the optimum temperature, a region with pore diffusion control in the neighbourhood of the temperature optimum, in which the reaction rate is strongly dependent on particle size, and a region above 1100 °C, which seems to be dominated by product layer diffusion.

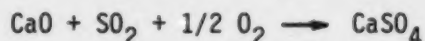
INTRODUCTION

This paper discusses the results of laboratory tests carried out at the University of Technology in Graz (Austria), to find out the fundamentals of flue gas desulfurization by dry limestone injection (1)(2)(3).

The dry limestone injection process uses finely ground limestone powders, which are fed into the boiler of a coal-fired power plant. There the calcium carbonate decomposes to lime by calcination:



The calcium oxide, which is formed by calcination, reacts with sulfur dioxide to form gypsum CaSO_4 in the presence of oxygen; this reaction is called sulfation:



Some special characteristics of the lime(stone) injection process are:

(1) High temperatures: Calcination and sulfation take place at high temperatures, ranging from about 1100 (1200) °C to below 800 °C; in this temperature-profile the solid particles are transported by the gases.

(2) At these high temperatures sintering takes place simultaneously with calcination.

(3) The solid particles leave the interesting temperature range after very short residence times (after 3 - 5 sec). In that short period most of the conversion takes place in a power plant boiler.

Both the strong sintering phenomena and the very short residence times are main obstacles against an improvement of the limestone injection process. Both lead to low calcium utilization (of about 10 or 15 %) of the limestone injection process, compared with the similar desulfurization by lime in a fluidization combustion power plant.

Parameters, which may play an important role in the limestone injection process, are: temperature, reaction time, particle-size distribution and mean diameter of particles, flue gas composition as percentage of SO_2 , O_2 and CO_2 , physical properties of the calcium additive - like pore structure and specific surface area, and, last but not least, also the quality of dispersing the powder (in connection with small particle diameters).

Although a great number of experimental investigations of reaction kinetics, have been conducted, e.g. (4) - (9), to mention just a few, contradictory explanations for their complex behaviour are given. Most of the investigations examined the reaction kinetics at reaction times of several minutes, at temperatures below 1000 °C and for larger particle sizes. The experiments of this paper therefore focused on reaction times of some seconds and temperatures above 1000 °C, which is close to the conditions of the limestone injection process.

EXPERIMENTAL

The SO_2 -capture was studied at short exposure times between 3 and 15 sec under isothermal conditions. The flue gas was produced by burning methane and adding SO_2 and extra CO_2 . The flue gas composition varied between 500-5000 ppm SO_2 , 2-8 vol% O_2 and 6-14 vol% CO_2 . The reaction temperatures were between 800 and 1200 °C.

The limestone particles are dispersed between the two sheets of a fleece of Al_2O_3 with a cross-sectional diameter of 50 mm - like a sandwich. The fleece is placed on the head of a sample holder, which looks like a pipe. The components and arrangement of the experimental setup, as well as the sample holder are described elsewhere (1)(3). A vacuum pump is connected to the pipe and causes the flue gases to flow through the fleece at a rate of about 4 m/s (e.g. at 900 °C). This flow rate related to the used diameter of the fleece (50 mm) and sample size was similar to that of (4). Therefore our trial installation represents a differential reactor - except that CO_2 was present in the flue gas during calcination, if one follows the argumentation of (10). The pipe is pushed into the stream of hot flue gas for the desired exposure times.

Most of the SO_2 -capture experiments were carried out with a 36/40 μm fraction and a sample size of 30 mg. Experiments were also conducted with sieve fractions of 5 μm -width, ranging from below less 5 μm to 90 μm to establish the influence of particle size on conversion. For the smaller sieve-fractions the sample size was less, e.g. for the 5/10 μm fraction it was 10 mg. The sieve fractions were characterized by BET-surface, as mentioned elsewhere (2)(3).

EXPERIMENTAL RESULTS AND DISCUSSION OF THE REACTION MECHANISM

SOME GENERAL REMARKS ON THE POROUS STRUCTURE OF THE SOLID REACTANT

First of all some general remarks on aspects of the reaction mechanism shall be made, so that we can better understand the experimental findings, discussed later on.

Gas/solid-reactions are characterized by the fact that the gaseous reactants, which are in our case SO_2 and O_2 , have to be transported to a reaction interface, which lies inside the particle and can shift towards the center of the particle during reaction. Therefore the SO_2 -capture has to be described as a combination of the transport of matter (e.g. by pore diffusion) and a chemical step.

Further we have to note that during the calcination of limestone, a lime develops, the porous structure of which depends upon calcination temperature and residence time. Therefore the solid reactant CaO can be appropriately described by a grain model and a pore model, respectively (see figure 1).

A salient aspect, we also have to account for, is that the sulfation reaction leads to decreasing pore diameters due to the formation of a shell of CaSO_4 -product around the CaO -grains or at the pore walls, respectively.

As a result of this porous structure the total reaction may include the following single steps:

- (1) Transport of the gaseous reactants by pore diffusion through the pores formed by calcination.
- (2) Diffusion to the reaction sites through the CaSO_4 -solid product shell, which is formed at the CaO -interface.
- (3) A chemical reaction step at the inner surface of the CaO (pore-walls).

PARTICLE SIZE EFFECTS

Due to the chemical step the reactant gases disappear towards the center of the particle, especially if the diffusion ways are long. The velocity of the chemical reaction step depends on the SO_2 -concentration at the actual reaction surface. Therefore the reaction may depend upon particle diameter.

Another situation we will find, if the chemical reaction step is very slow - with regard to the pore diffusion step: SO_2 and O_2 will be rapidly transported to the reaction surface, and the same flue gas concentrations will exist within the porous structure of the calcined particle as in the surroundings of the particle, leading to a homogeneous reaction in the particle. The total rate of the SO_2 -capture should not depend on the particle diameter.

SEVERAL CHEMICAL REACTIONS AND SINTERING PROCESSES

The few above-mentioned steps would suffice to give a very complex relationship between the extent of reaction and temperature, reaction time, diameter of particles, SO_2 -concentration and so on.

Yet the $\text{SO}_2/\text{CaCO}_3$ -reaction is even more complicated because additionally we have to take account of the following chemical and sintering steps:

- (1) calcination (decomposition of CaCO_3 to CaO)
- (2) formation (sulfation) of a calcium sulfate-shell (CaSO_4) around the CaO -grains or pore-walls, respectively,
- (3) formation of calcium sulfite (CaSO_3) in the first 1.5 seconds,
- (4) decomposition of CaSO_3 ,
- (5) sintering processes in the CaO -core of the CaO -grains,
- (6) sintering processes in the CaSO_4 -shell.

The formation of sulfite - mentioned above - is clearly illustrated e.g. in the experimental work of (5) or (6). In (5) it is shown that formation of sulfite is related to the endothermic calcination reaction, by which the inner temperature of the particles may be lowered for a short time - in comparison with the temperature of the surrounding flue gas atmosphere.

The redecomposition of CaSO_3 begins after some tenths of a second (5), when the calcination is almost complete, and leads to a stronger O_2 -dependence at shorter reaction times. The latter is an interesting phenomenon, which was observed by us, but shall be discussed in a later paper.

What we want to emphasize, is that the formation of sulfite provides strong evidence for the argument that a chemical step (probably the oxidation step) is rate-controlling at lower temperatures.

In this paper we want to deal primarily with the sintering processes, which were found to have a dominating influence upon the observed relationship between reaction velocities and temperature.

SINTERING EFFECTS

Sintering processes will set in at the so-called Tammann-temperature, which characterizes the beginning of sintering and is usually 0.4-0.5 times the melting point on the absolute temperature scale (13).

CaO has a relative high melting point of 2614°C (2887 K) and although sintering processes will increase exponentially with temperature, one would not normally assume that they will markedly influence the reaction in the examined range of temperatures, especially within the short reaction times. But we have to take account of a special influence of CO_2 on sintering phenomena in the CaO -solid phase, which is well-documented in the calcination literature (11, 12):

If higher CO_2 -concentrations are present, the sintering of the solid reactant CaO takes place sufficiently fast to affect the absorption of SO_2 . Such higher CO_2 -pressures exist in the particle:

- (1) When the CO_2 -concentration in the surrounding flue gas is high.

- (2) During the calcination process. Then high CO_2 -pressures develop in the particle by the decomposition of limestone.

As our calcination experiments show, there is a rapid decrease of the BET-surface with increasing calcination temperatures and calcination times (figure 2). (In the presence of atmospheric humidity the CaO partially reacted to form Ca(OH)_2 after

sampling. The surfaces of 100 % CaO, which are shown in figure 2, had to be estimated from measured surfaces, from the actual extent of reaction to $\text{Ca}(\text{OH})_2$, and from the surfaces of two samples, which had completely reacted to form $\text{Ca}(\text{OH})_2$.

The effect of these sintering processes can be twofold: It can both decrease and increase the reactivity of CaO:

(1) On the one hand sintering processes in the solid reactant CaO lead to a reduction of the (inner) surface, as figure 2 showed, and thereby to a loss of reactivity.

(2) On the other hand, this decrease of the surface is accompanied by an increase in the mean pore diameter, up to temperatures of about 950 °C - according to (7) - and therefore results in a coarsening of the pore structure. This is an advantage, when at higher temperatures the chemical step becomes rapid and hence pore diffusion begins to influence the reaction velocity.

(3) However at temperatures above 950 °C - according to (7, 8) - the total porosity will decrease and result in a decreasing mean pore diameter. This is disadvantageous to the reactivity.

(4) Finally we have to take account of sintering processes in the CaO, which may promote the formation of cracks in the CaSO_4 product layer, when they continue during the reaction with SO_2 . This will be advantageous to the reactivity.

Figure 3 shows how one may imagine that crack formation as a combined effect (co-operation) of both solid phases. In case the porous CaO-phase sinters (or shrinks) more intensively than the CaSO_4 -layer (e.g. in the presence of a higher CO_2 -partial pressure), we suppose that a stronger formation of fissures will occur in the CaSO_4 -layer. This formation of cracks advances the reactivity, because the gaseous reactants have better access to the reaction site (CaO-interface).

The promoting effect of CO_2 was observed, when extra CO_2 was added to the flue gas. We obtained a higher SO_2 -capture at temperatures above 1000 °C (figure 4). Probably the same mechanism causes the better SO_2 -capture, which we observed during calcination, when high CO_2 -pressures due to decomposition of CaCO_3 exist in the particle (figure 5). When calcination ceases, the SO_2 -capture also stops.

CONTROLLING STEPS

In order to simplify the interpretation of experimental results, one commonly searches for the so-called controlling step. This should be a single step - like a local chemical reaction step at the reaction interface (between the two phases CaO and CaSO_4) or a step of transport of matter (e.g. pore diffusion), which dominates the reaction mechanism and therefore mainly influences the total velocity of the reaction: The velocity of that single step should be approximately equal to the total velocity of the SO_2 -capture.

On the basis of our experimental results we are able to postulate the following rate controlling steps, dependent on the temperature range:

- (1) temperatures between below 800 up to 900 °C: chemical control
- (2) temperatures between 900 - 1100 °C: pore diffusion control
- (3) temperatures above 1100 °C: product layer diffusion control.

Especially when both temperature and particle diameter were varied in our experiments, we obtained results, which call for such an interpretation. These three regions can be clearly recognized, as figure 6 shows:

Depending on the temperature range an influence of the particle size is observed or not observed. As stated above, particle size effects depend on the relative rates of the chemical step and the pore diffusion step, respectively. Together with other effects this phenomenon allows us to narrow down the possible prevailing rate controlling steps, as was mentioned before.

Sintering processes, which depend upon temperature, CO_2 -concentration and exposure time, have a substantial effect on the controlling step.

Chemical control at temperatures in the range between 800-900 °C

Generally chemical control predominates at lower temperatures (13).

By sintering of the CaO the chemical control spreads to even higher temperatures than one would normally expect: The total (BET)-surface, which decreases by sintering, can be related to the inner reaction surface. Therefore the effective velocity of the chemical reaction step will decrease too, and control the total reaction rate. Moreover, the pore system within the CaO will shift to larger pore diameters, and therefore will suffice for transport of matter (by pore diffusion) in spite of decreasing pore diameter effects due to the formation of a solid product layer at the pore walls.

When we regard a porous particle, chemical control (slow chemical step) is characterized by the fact that no influence of the particle size exists (13).

Therefore in our case (compare figure 6) chemical control may prevail at temperatures below 900 °C: In this temperature range no or only a very weak influence of the particle size on conversion is observed. (The weak dependence on particle size may appear as a result of the simultaneously occurring calcination, which is also affected by the particle size).

An Arrhenius-plot of the velocities of conversion to CaSO_4 yields straights in the range of temperatures < 950 °C (figure 7).

Pore diffusion control at temperatures in the range between 900-1100 °C

Another reaction mechanism becomes evident in the temperature range between 900 and 1100 °C, in which also the temperature optimum lies.

In the region of the temperature optimum and at somewhat higher temperatures a strong particle size influence is manifest (see figure 6). This pronounced dependence of the conversions upon particle size is also shown in figure 8 for a temperature of 1070 °C. This is undoubtedly a case of pore diffusion control.

At the same time this is the temperature range, in which in the furnace of a power plant the SO_2 -capture by dry limestone injection mainly takes place. Chemically analysed sieve fractions of ashes from different power plants with furnace limestone injection therefore also show a strong dependence of the conversions upon particle size (figure 9).

In this temperature range (900-1100 °C) the rate of the chemical step increases exponentially with temperature and finally becomes more rapid than pore diffusion, which increases only slightly with temperature. Then the transport of matter within the pores becomes limiting.

Yet the exact conversion/temperature relationship, as shown in figure 6, has to be explained in more detail at this point. Pore diffusion control in the purest form (e.g. considered as a phenomenon of its own without regard to sintering or other effects) - above all - just would mean that the reaction rate cannot increase exponentially at any value, but achieves de facto only a maximum value. Beyond this value an additional rise in the temperature would only result in an insignificant further increase in conversions to CaSO_4 .

The strange decrease in conversions at higher temperatures therefore must be the result of other effects. According to our observations sintering effects are assumed to be predominantly responsible for this decrease in conversions. The influence of the pore system and the characteristic pore diameter, respectively, is also reflected in the complex situation, which we found in regard of the temperature optimum:

The temperature optimum shifts with reaction time and conversion, respectively (figure 10). This phenomenon seems to be caused by the narrowing of the pores, which is due both to

- (1) sintering phenomena, which increase with increasing temperature,
- (2) and to the formation of a solid product layer at the pore wall surfaces with progressing conversion of CaO to CaSO_4 (figure 11).

Since the developing CaSO_4 -product layer also results in a narrowing of the pores, the temperature optimum becomes dependent on the conversion: The transition between chemical control and pore diffusion control shifts to lower temperatures.

Product layer diffusion control at temperatures above 1100 °C

In larger particles, under the control of pore diffusion, a thicker CaSO_4 -product layer develops in the pore mouth region near the outer particle surface, even if the total conversion reaches only moderate values.

In this zone of the thicker calcium sulfate-product layer, diffusion through the product layer (which occurs in cracks of the layer) soon influences and therefore slows down the reaction. For longer reaction times the concentration profile within the particle diminishes, and the total conversions become less dependent on particle-size with rising temperatures (figure 6).

Earlier on it was pointed out that in the presence of higher CO_2 -(partial)-pressures sintering phenomena in the solid reactant CaO may endure for longer times and then lead to the formation of cracks in the adherent CaSO_4 -product layer. Therefore the CO_2 -partial pressure in the flue gas is of importance for the just mentioned transition between pore diffusion control and product layer control, or it is of importance, as long as calcination occurs simultaneously with the SO_2 -capture.

At high temperatures above 1100 °C calcination and sintering processes in the CaO -phase take place rapidly and completely. This results in a tight calcium sulfate covering at the pore walls without any cracks. Moreover, since the calcium sulfate layer also shows a rapid sintering rate at these temperatures, eventually formed cracks will heal up very quickly. Then, at longer exposure times, solid state diffusion control through the product layer establishes and ends in a very drastic reduction of the reaction rate. Therefore at temperatures beyond 1100 °C the reaction apparently reaches a deadlock at reaction times above 5 sec.

CONCLUSIONS FOR THE LIMESTONE INJECTION PROCESS

From the aforesaid we have seen that in the temperature range, in which the main part of the flue gas is desulfurized by the LI-process, especially two (partial) steps control the total reaction:

- (1) pore diffusion (for temperatures between 900 - 1100 °C)
- (2) product layer diffusion (which becomes rate controlling at temperatures above 1100 °C).

For the application in practice some significant conclusions can be drawn:

(1) Pore diffusion control is characterized by a strong influence of particle size on conversions. Therefore it is important to choose an optimum particle size. In particular fine particles of $< 10 \mu\text{m}$ allow substantially higher conversions.

(2) As our experiments show, one has to ensure that the particles are properly dispersed, especially if one uses fine particles. Yet this problem of agglomerates, which behave like larger particles in a reaction, has so far been mostly neglected, - with only a few exceptions, e.g. (14). Further scientific work would be of interest and great importance in this field.

(3) As our tests show, sintering processes in the CaO -phase can also promote reactivity, because they presumably lead to formation of cracks in the CaSO_4 -product layer. Therefore it is desirable that these sintering processes occur as long as possible simultaneously with the SO_2 -capture. However, in practice they proceed too quickly, when raw uncalcined limestone is used as an additive. We attribute this to high CO_2 -pressures, which develop in the particle during CaCO_3 -decomposition.

Therefore an improvement in the LI-process maybe could consist of precalcinating limestone or calcium hydroxide - completely (or at least 90 %) - to high surfaces in a CO_2 -free atmosphere, before using them as additives. On the other hand a partial calcination (60-80 %) to high surfaces ($\geq 40 \text{ m}^2/\text{g}$) will not succeed, as the experiments of (15) show. As it can be concluded from sintering tests carried out by other authors (e.g. 10, 11, 12), this must be due to the CO_2 -development by the decomposition of residual CaCO_3 , which takes place even in partially calcined stones. Yet at calcination conversions above 90 %, complete calcination will proceed only at a very slow rate and hence release only little CO_2 .

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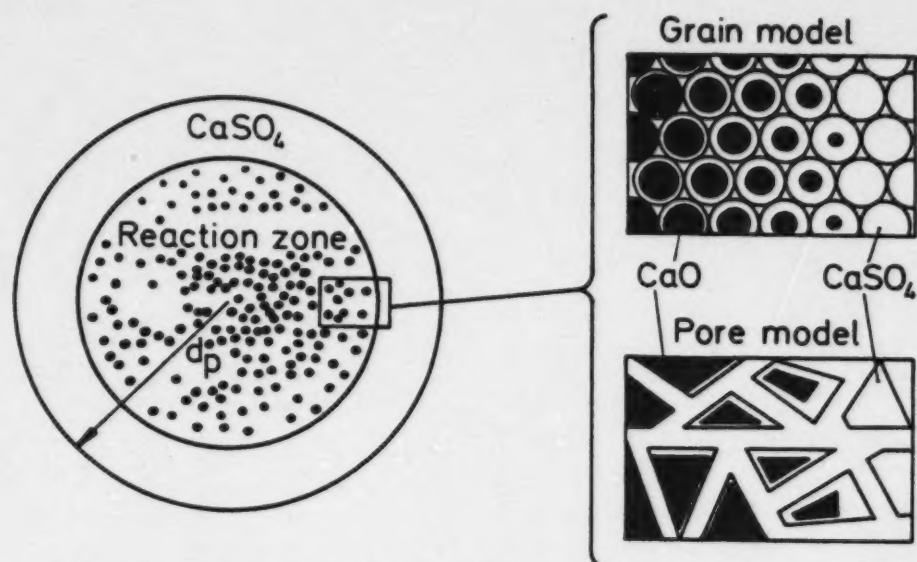


Figure 1. Porous structure of calcined lime particles (CaO) as represented by grain model and pore model, respectively.

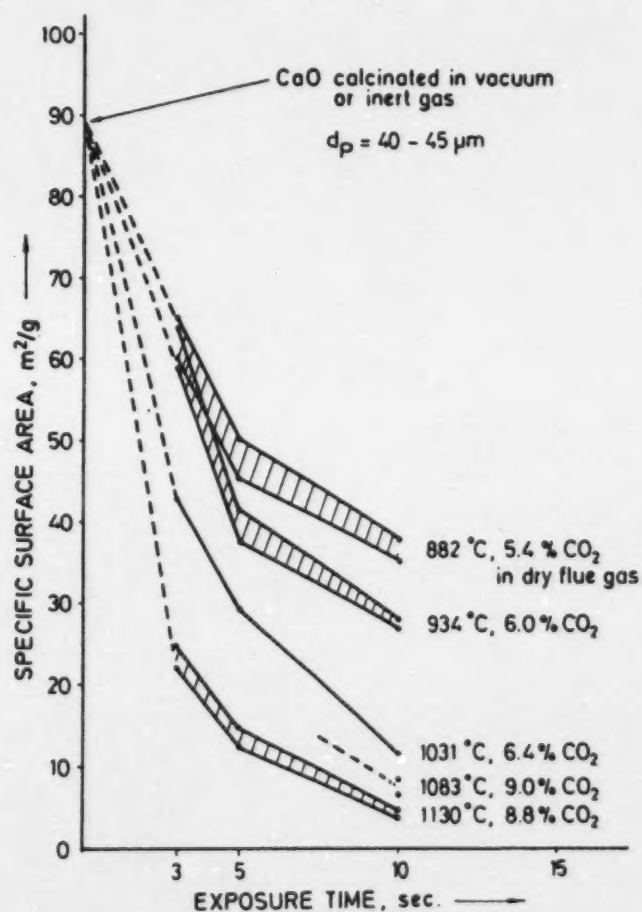
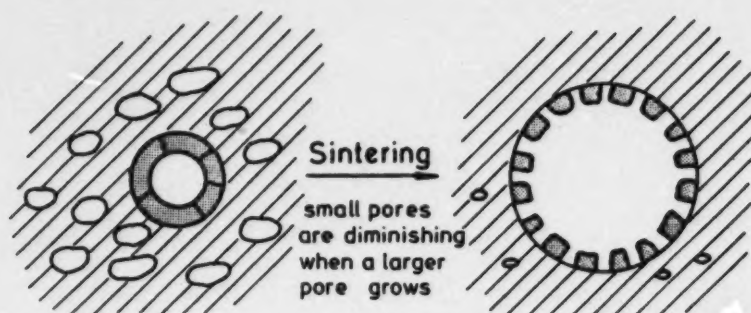


Figure 2. BET-surfaces of CaO after calcination - depending on temperature and exposure time, extrapolated for a 100 % CaO -conversion.

PORE MODEL :



GRAIN MODEL :

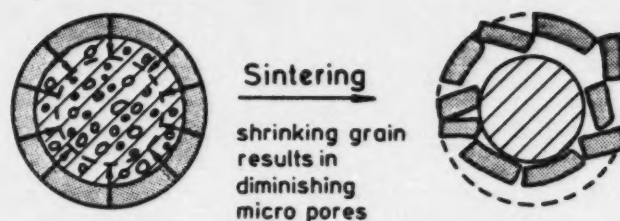


Figure 3. Crack formation in the CaSO_4 -solid product layer due to sintering processes in the adherent CaO -phase; schematized for a grain model and a pore model, respectively.

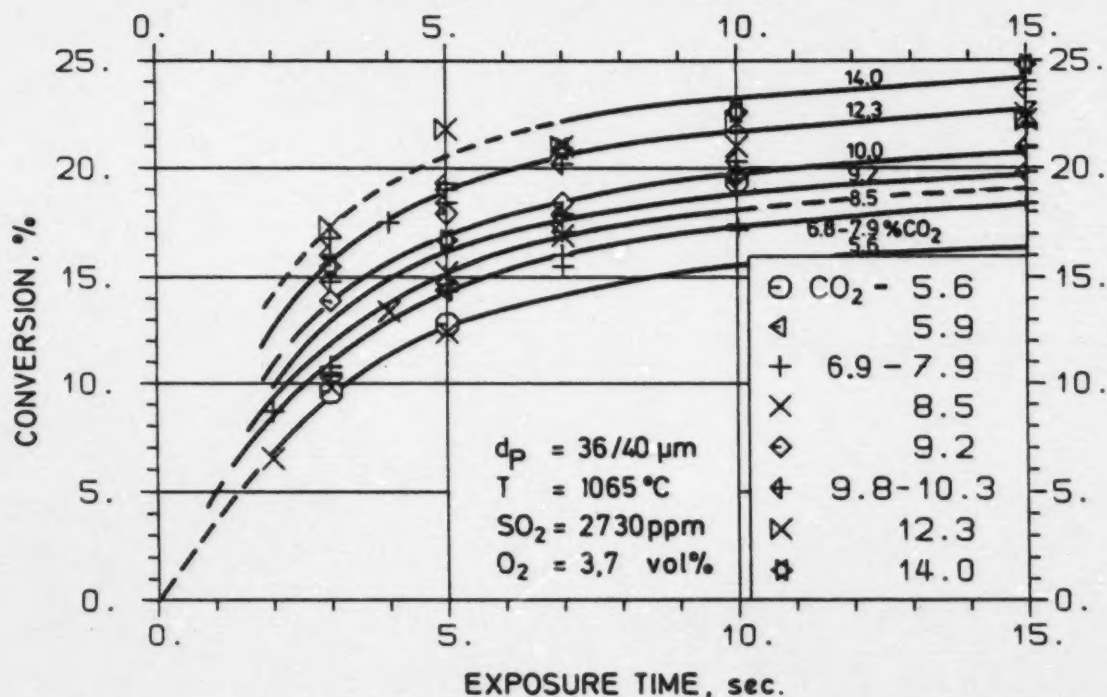


Figure 4. Advancing CO_2 -influence upon conversion of CaO to CaSO_4 for $T = 1065^\circ\text{C}$.

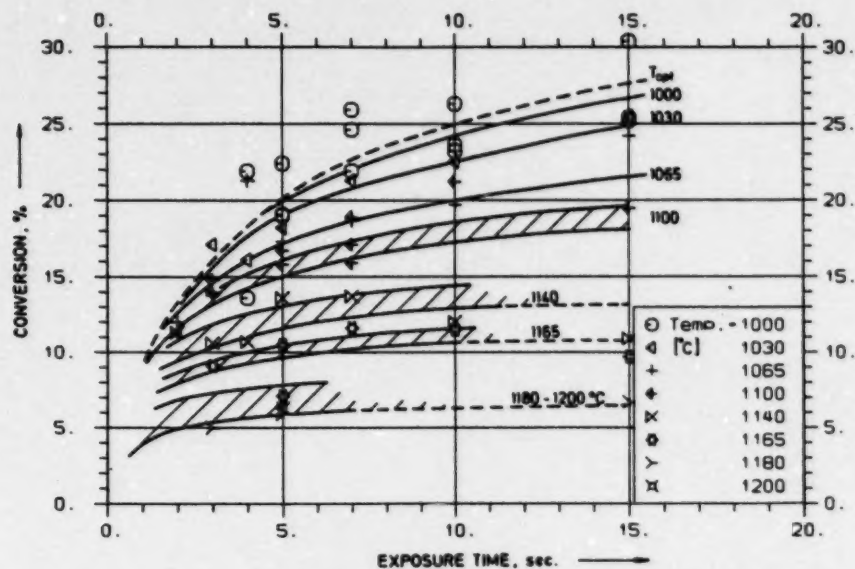


Figure 5. Typical conversion/time-profiles at high temperatures (fast calcination).

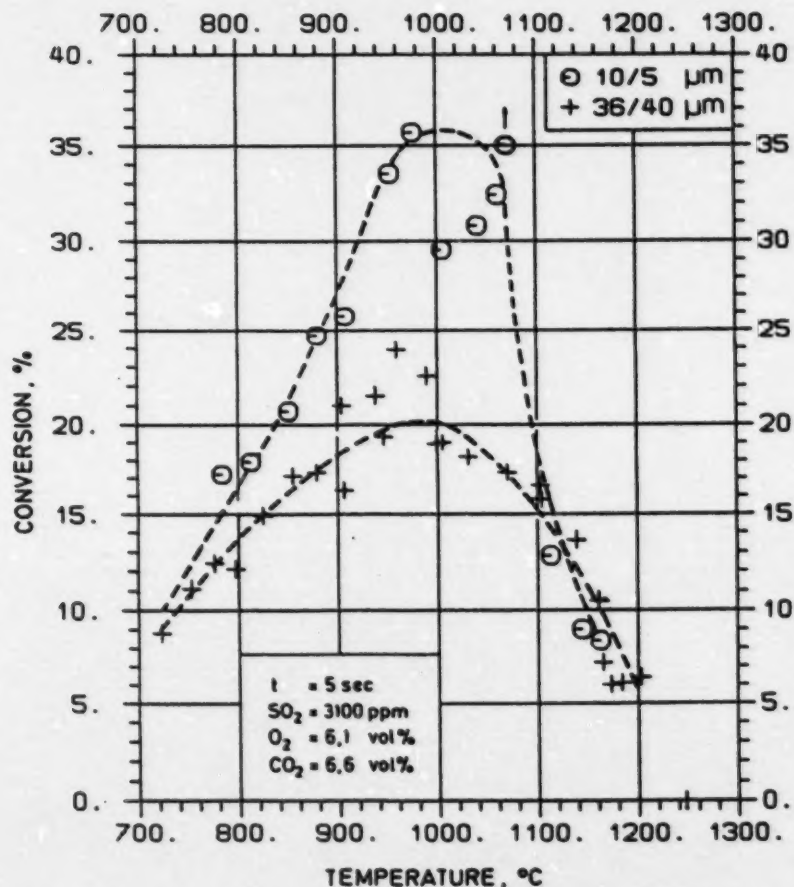


Figure 6. Conversion/temperature-profiles for two different sieve fractions (5/10 μm and 36/40 μm); reaction time = 5 sec.

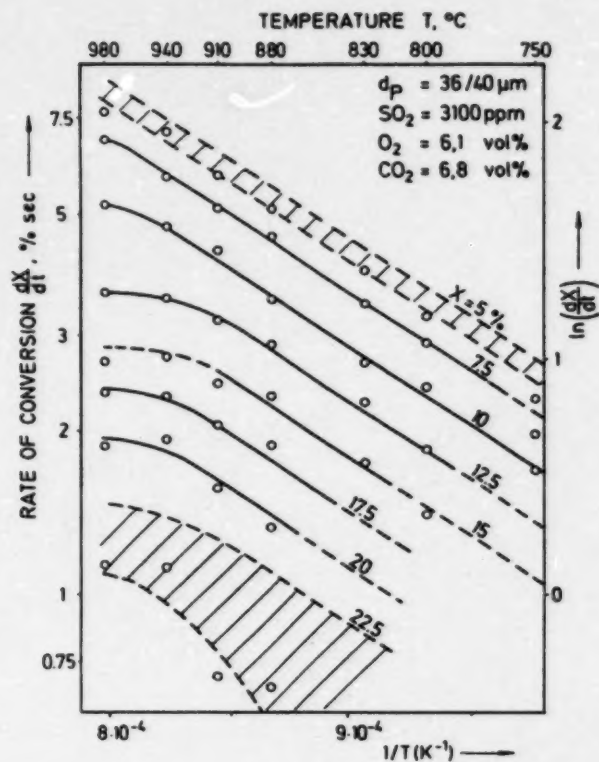


Figure 7. Arrhenius plot of reaction rates for different constant conversions.

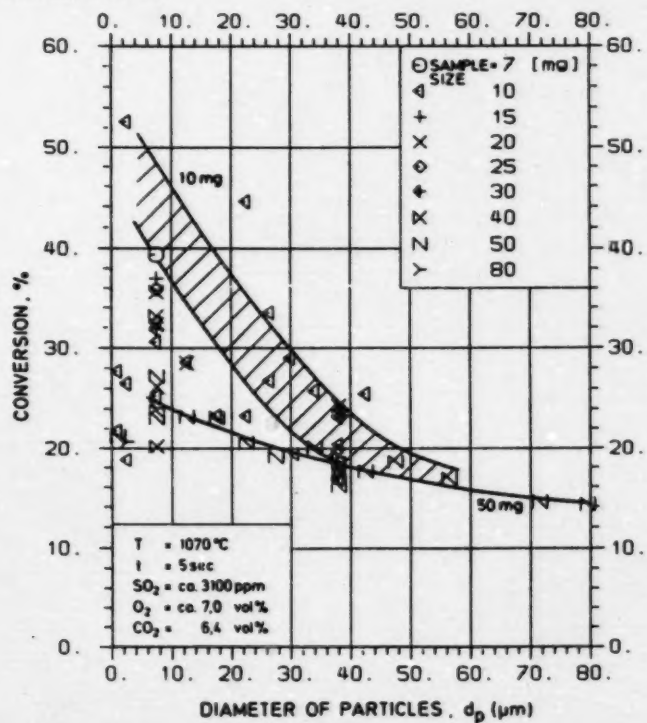


Figure 8. Particle size influence upon conversion at a temperature of 1070 °C.

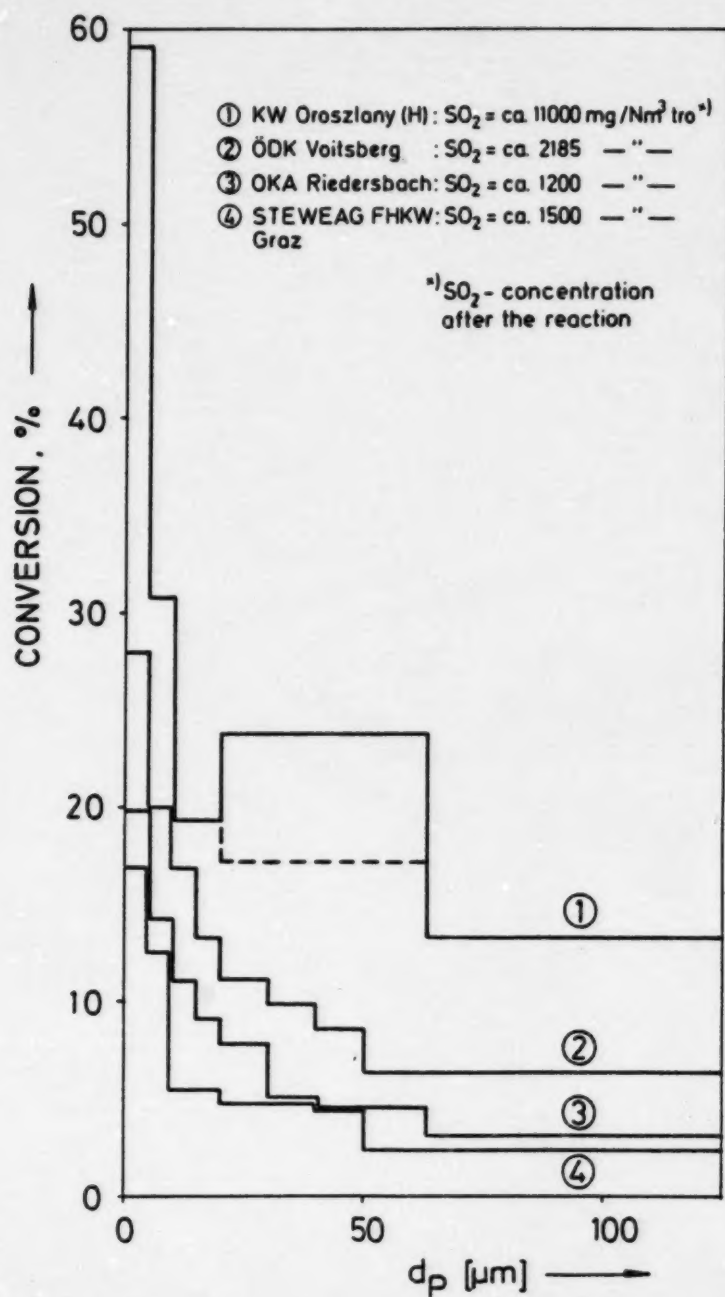


Figure 9. Extent of sulfation (conversion) of sieve fractions of LI-ashes from different power plants.

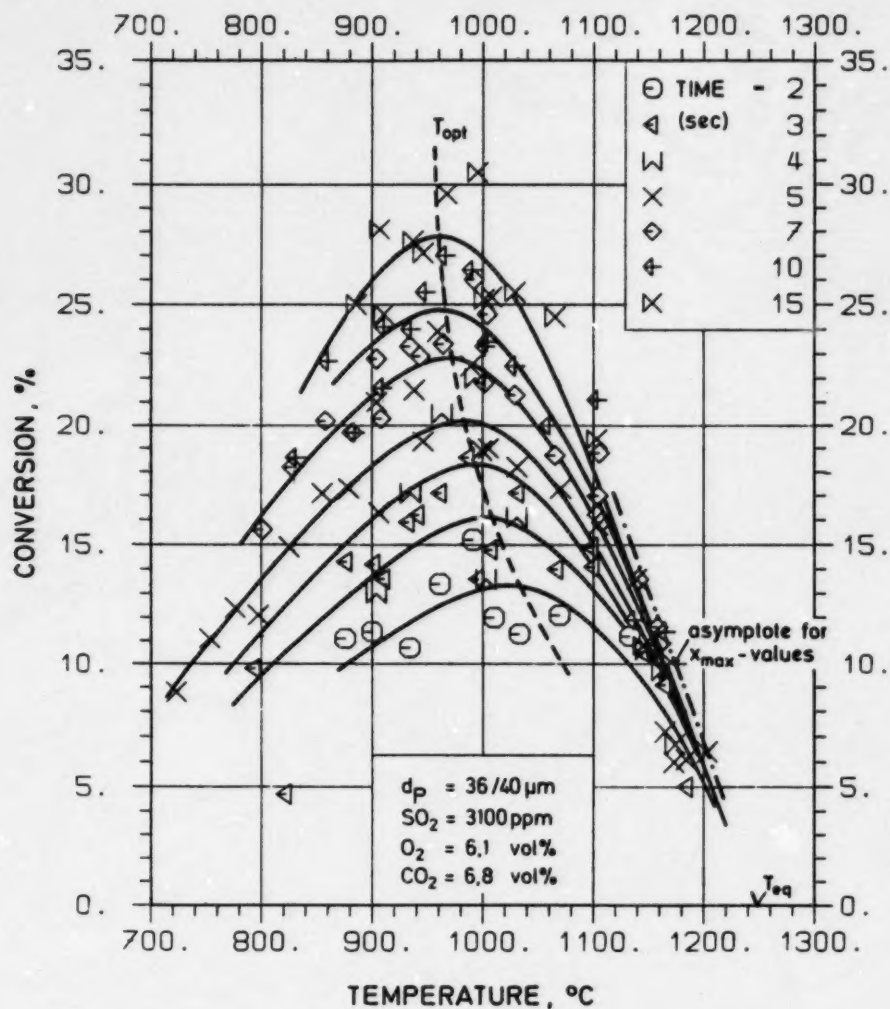


Figure 10. Temperature optimum depending on reaction time and conversion, respectively.

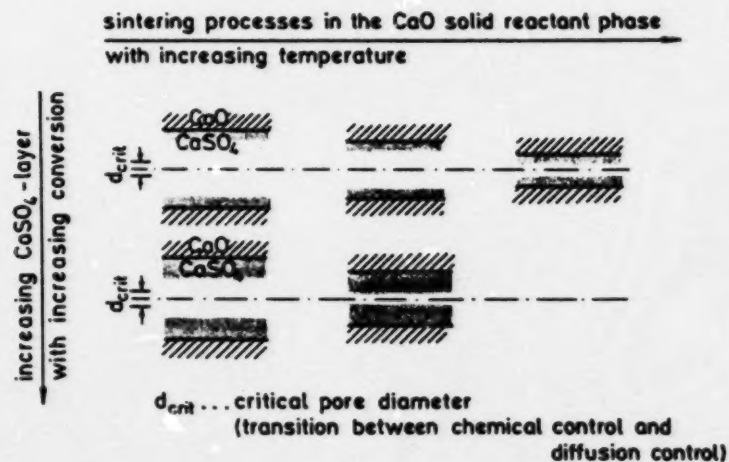


Figure 11. Pore diameters decrease both by sintering processes and by the formation of a solid product layer.

SURFACE CHEMICAL REACTIVITY OF DIFFERENT CALCIUM BASED SORBENTS WITH SO₂

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ABSTRACT

The reactivities of calcium based sorbents obtained from CaCO₃ (c-CaO) and from Ca(OH)₂ (h-CaO) vs SO₂ have been proved to be different. This behavior might be due both to microstructure and to surface chemical reactivity of the sorbents.

The aim of this work is to present preliminary studies performed by X-ray Photoelectron Spectroscopy on the role of the surface chemical reactivity of c-CaO and h-CaO vs SO₂ at 298 K.

A careful analysis of the chemisorption process demonstrates that the formation of strong bonds among Ca-O-S is enhanced on c-CaO surfaces, while a double adsorption mode is possible on the h-CaO surfaces.

INTRODUCTION

The reaction of calcium oxides with SO₂ has been extensively studied both theoretically and experimentally because of its importance in pollution control technologies (1).

It has been pointed-out that the sorbent microstructure (porosity, grain size and surface area) can take an important role in the desulfuration process (2, 3). CaO microstructure can be designed selecting proper precursors and proper

processing conditions. When long distance diffusion steps can be neglected the CaO from CaCO_3 (c-CaO) has pores with cylindrical symmetry, while the CaO from Ca(OH)_2 is characterized by cavities of planar symmetry (4). These features might indeed affect the high-temperature reactivity behavior of CaO vs SO_2 providing that no further steps are acting in the course of the reactions. Unfortunately, because of the high probability of sintering processes (due to the presence of CO_2 (5) and $\text{H}_2\text{O(v)}$ (6)), the sorbents can change as the reaction proceeds. Sometimes no clear correlations have been found between reactivity and microstructural properties of the initial sorbents probably because of the summation of the earlier mentioned processes. However the development of the microstructural studies have stimulated activities of research and development oriented to design a sorbent characterized by fine particle size and resistance to the sintering during the calcination process (7).

In this framework the design of proper sorbents needs information on the surface properties and reactivity of the precursor materials beside the microstructural ones. Calcium oxides from different sources could have different reactivity vs SO_2 not only because of grain size, porosity and surface area, but also because of the chemical states of their surface atoms.

Within the research project RIDOX, carried out in Italy under the supervision of the Italian Electricity Board, ENEL, we have studied the surface chemical reactivity of two kinds of CaO vs SO_2 . The first one is a h-CaO single-crystal reconstructed by heating in vacuo a Ca(OH)_2 surface previously obtained by the hydration in air of a CaO single crystal, while the second one is c-CaO produced from a CaCO_3 single crystal decomposed in high vacuum at 950 K.

EXPERIMENTAL PART

A. Sample preparation

A CaO single crystal cleaved along (100) face and exposed to air, and a CaCO_3 natural crystal were used in this work. The samples were mounted on a resistively heated holder and annealed at 900 K in vacuo in order to obtain a CaO surface. Only on the c-CaO surface a very small amount of carbon was revealed by Auger electron spectroscopy. The clean surface were then exposed, at room temperature, to SO_2 at a partial pressure of about 10^{-4} Pa. After each exposure the S-2p, O-1s and Ca-2p core level lines were recorded by XPS.

B. Apparatus

All the experiments were performed in a standard ultra high-vacuum (U.H.V.) system which consists of two stainless steel chambers (the analysis and the preparation chamber) separated by a metallic valve. Samples transfer from the analysis chamber to the preparation chamber and vice-versa, is allowed by means of a magnetic rod. Both the chambers are evacuated by a combination of ion and liquid nitrogen cooled titanium sublimation pumps. Base pressures of 10^{-5} Pa and 10^{-7} Pa can be routinely reached in the analysis and in the preparation chambers respectively.

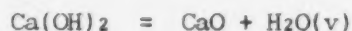
The preparation chamber is equipped with a home-made sample holder manipulator which allows the sample to be heated up to 950 K. Gases are admitted in the preparation chamber through a leak-valve system. The analysis chamber is equipped with an electron hemispherical analyser (Leybold-Heraeus, model Ea10:11) operating in both $\Delta E/E = \text{const}$ and $\Delta E = \text{const}$ mode, an ion gun, an electron flood gun and a X-ray source (twin anode for Mg and Al $K\alpha$ lines) and a X,Y,Z, θ manipulator.

RESULTS AND DISCUSSION

Crystallographic planes (100) of CaO single-crystals quickly adsorb $\text{H}_2\text{O}(\text{v})$ at 298 K which forms on the surface $\text{Ca}(\text{OH})_2$ groups (9). The binding energy of the relative O-1s core levels line is found at 533 eV.

After heating in vacuo at 873 K for 1 hour the CaO structure is restored, as shown by the O-1s and Ca-2p core level lines reported in Figure 1a and Figure 2a, which exhibit features typical of pure CaO crystals. Therefore the XPS spectra shown in Figure 1a and Figure 2a might be related to surface chemical states of h-CaO.

However, even if a direct proof of the $\text{CaO} \rightarrow \text{Ca}(\text{OH})_2$ transformation is not given in the present experiment, by comparing the XPS spectra of pure CaO and $\text{Ca}(\text{OH})_2$ we have evidence that this transformation is definitely reversible. That is in agreement with the conclusion derived from the topotatic reaction in vacuum:



according to which the rearrangement of the lattices due to the molar volume changes should imply namely movements of atoms along the [111] CaO direction leaving the atoms on the surface almost in the same position (4).

Injection of SO_2 at 298 K and at a pressure of 1.3×10^{-4} Pa into the reacting chamber yields surface products whose nature can be clarified from the chemical-surfaces states of the oxygen, sulfur and calcium atoms.

When h-CaO interacts with SO_2 the S-2p XPS spectra exhibit two chemical states which gradually evolve as the coverage increases. Particularly two peaks at 169 eV and 170.5 eV can be identified, see Figure 3(a-f). However it should be noticed that at low coverages only the peak at 169 eV can be detected, while the other becomes evident at exposure higher than about 100L. At exposures between 10^3 and 10^4 L the process reaches its saturation and no more sulfur is gettered by the CaO surface.

After annealing the sample in vacuo for 1 hour at 923 K the peak at 169 eV disappears, indicating a weaker bond state of the SO_2 on the CaO surface. A possible explanation can arise from the fact that the apparent activation energy for this step is lower than that of the stronger bonded state. This mechanism is clearly due to the presence on the CaO surface of competing sites(10). Differently the interaction of SO_2 with c-CaO, under the previous conditions (298 K and 1.3×10^{-4} Pa), induces (Figures 4 (a, b)) only one S-2p line, at 168.5 eV, which does not disappear after annealing at 923 K.

The different XPS behavior of the sulfur atoms adsorbed on the h-CaO and on c-CaO surfaces can be perceived from the evolution of XPS spectra connected with the oxygen and calcium atoms of the correspondent oxides. In the h-CaO oxide both O and Ca change significantly their surface chemical states as the SO_2 adsorption proceeds. As Figure 1 (a-f) illustrates, the main line for the oxygen gradually reduces its intensity. A new peak appears around 533.2 eV and it becomes the main line when the degree of coverage is equal to 10,000 L. An intensity decrease of the Ca-2p peaks is also observed, while new lines appear at about 353 eV and about 349.5 eV, see Figures 2 (a-f), indicating the formations of new Ca bonds. On the contrary O-1s and Ca-2p spectra measured on c-CaO surface do not change substantially their binding energy as SO_2 is adsorbed, as reported in Figure 5(a-b) and Figure 6(a-b). Nevertheless XPS spectra of the S 2p core levels show unambiguously a strong interaction between SO_2 and CaO surface.

A possible interpretation of this behavior can arise from the fact that bonds between the active sites of the CaO surface and the SO₂ molecules on the c-CaO surfaces do not require extra activation energy, as the active sites of the h-CaO surface do. In a way the O and Ca sites on c-CaO surfaces seems to be in an energy configuration that minimizes the activation free energy barrier to form stable bonds between calcium, oxygen and sulfur atoms. Since this is not the case for O and Ca atoms on h-CaO surfaces a double mode of accomodating the sulfur becomes possible.

The chemical nature of stable Ca-O-S bonds might be related to the formation of bidimensional CaSO₃, which is a thermodynamically allowed reaction between CaO and SO₂ at 298 K (11).

The XPS analysis above illustrated leads therefore to the conclusion that the formation of strong bonds between calcium, oxygen and sulfur atoms is facilitated on c-CaO surfaces at 298 K. Furthermore the species formed are stable at least up to the temperature of 923 K. If calcium oxides from hydroxides would behave as the h-CaO here used, then the oxides produced from endothermic decomposition of Ca(OH)₂ would adsorbe SO₂ according to a different mechanism.

Preliminary experiments carried out at higher temperature (12), suggest that even if the final adsorbed species are the same the kinetic of adsorption is different at c-CaO and at h-CaO surfaces.

Finally the formation of sulfite and/or sulfate on the CaO surface does not correspond necessarily to the behavior of a proper sorbent. Indeed the simultaneous presence of sulfite and sulfate might enhance the formation of low melting liquid phase which will rule-out the role of the pores and the surface area.

The work described in this paper was not funded by the U. S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

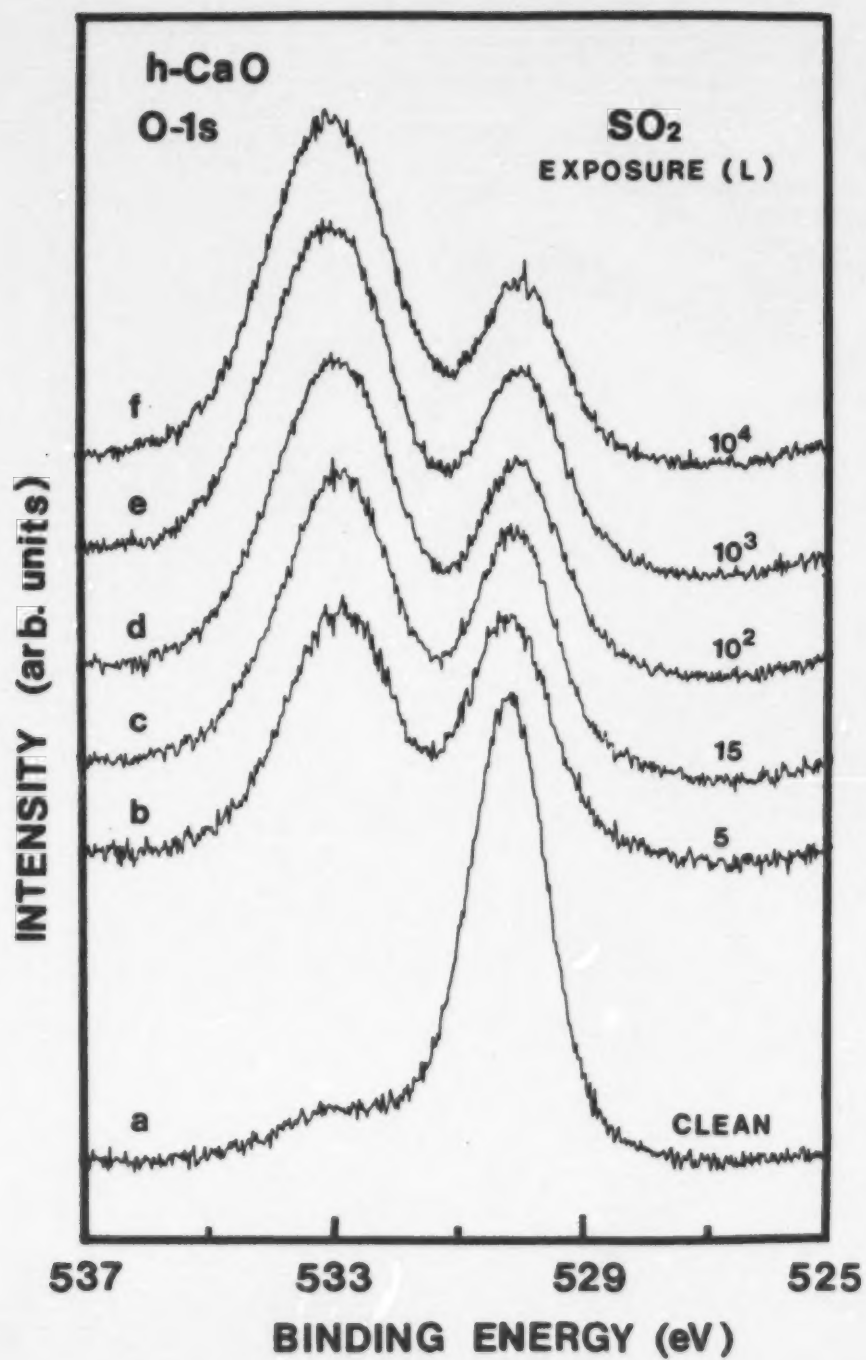


Figure1. XPS spectra of O-1s core levels for h-CaO surface exposed to SO₂.

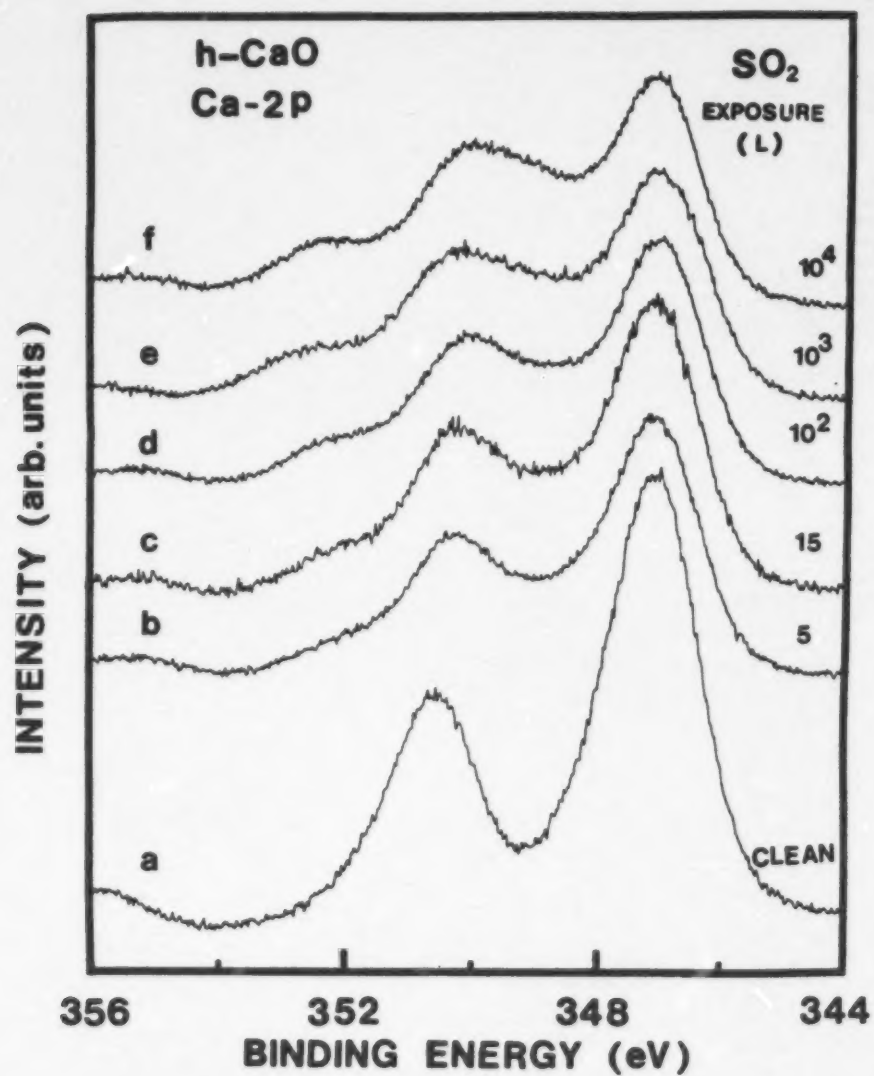


Figure 2. XPS spectra of Ca-2p core levels for h-CaO surface exposed to SO₂.

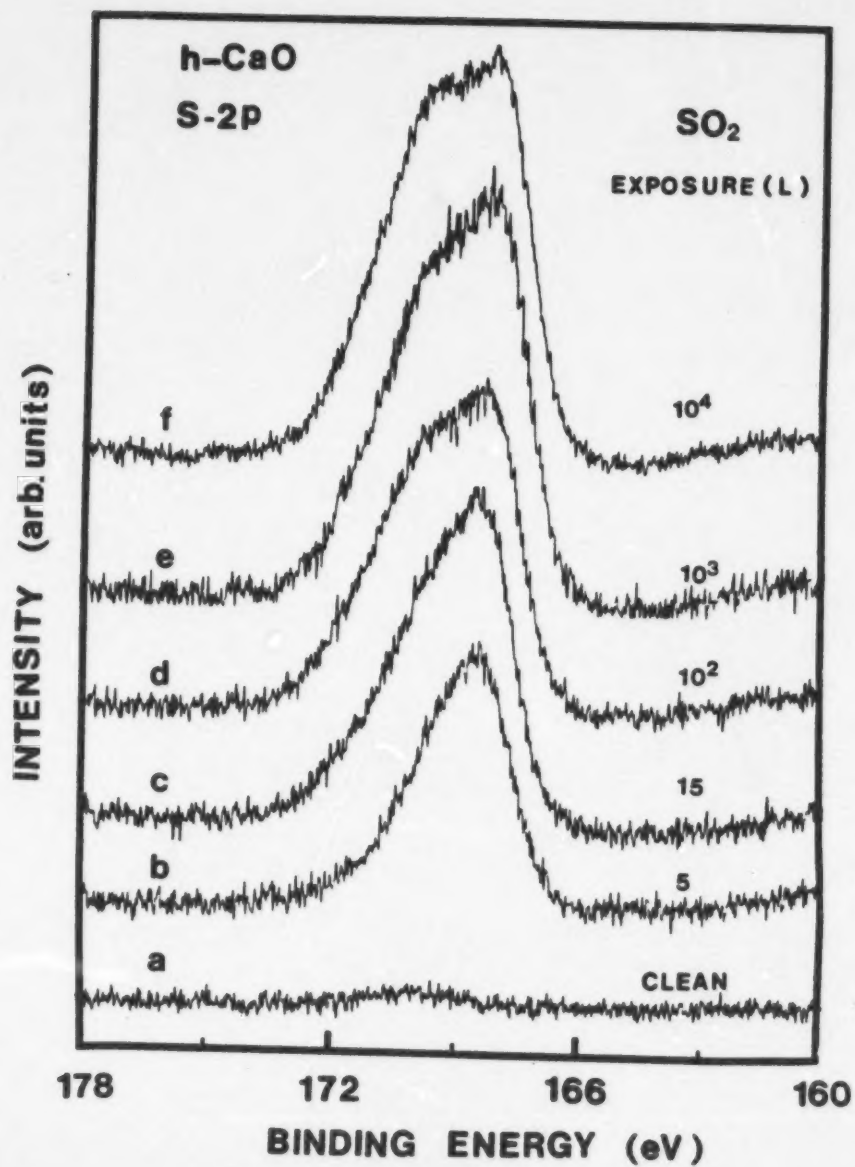


Figure 3. XPS spectra of S-2p core levels for h-CaO surface exposed to SO₂.

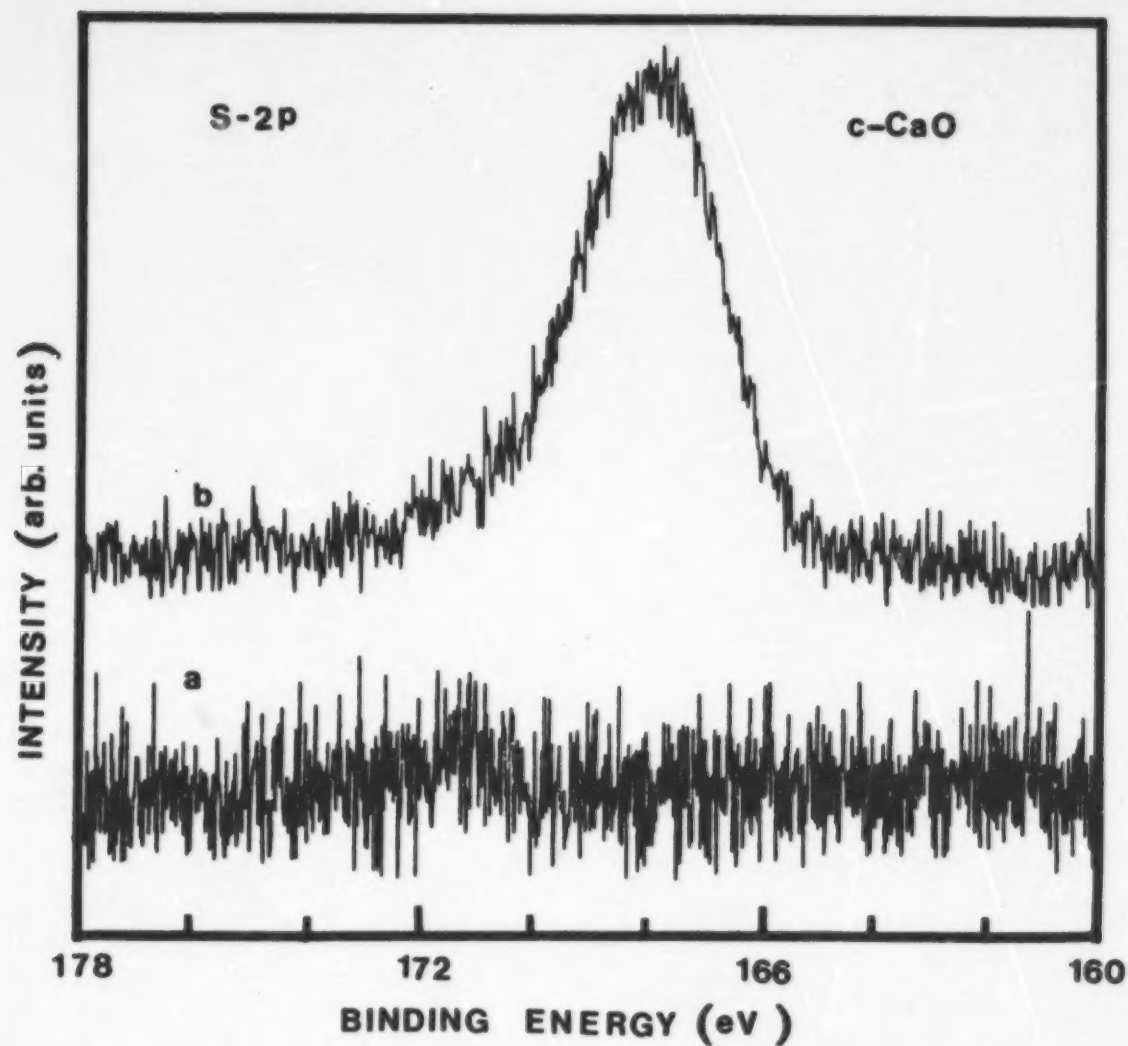


Figure 4. XPS spectra of S-2p core levels for $c\text{-CaO}$ surface; a) clean surface, b) surface exposed to 4.5×10^4 L of SO_2 .

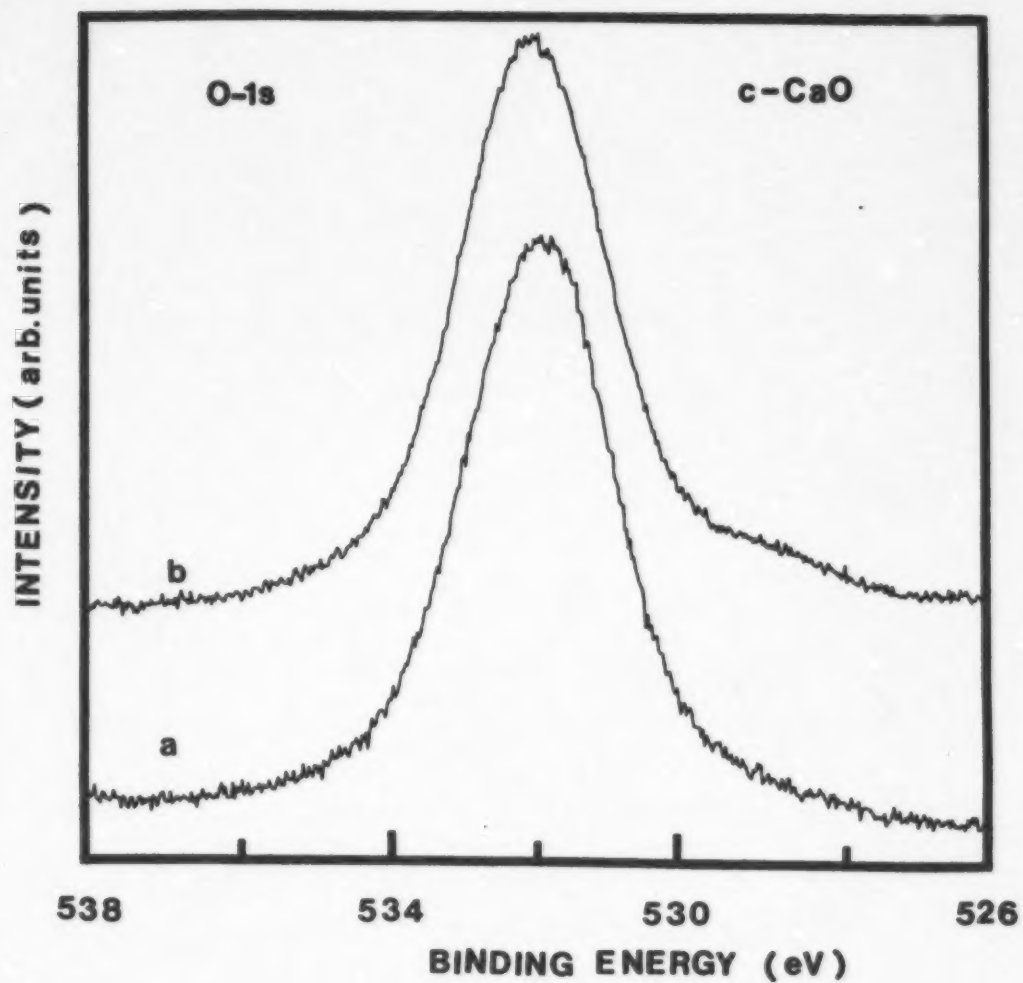


Figure 5. XPS spectra of O-1s core levels for c-CaO surface; a) clean surface, b) surface exposed to 4.5×10^4 L of SO₂.

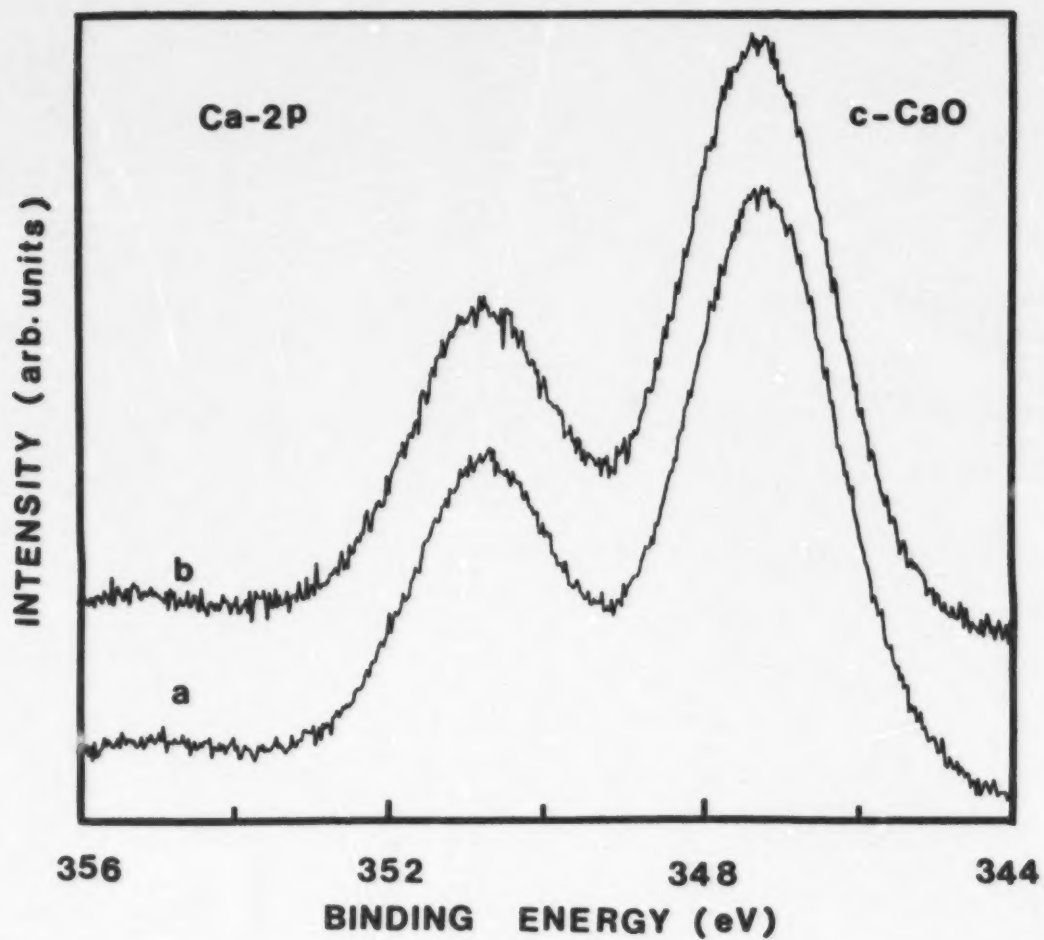


Figure 6. XPS spectra of Ca-2p core levels for $c\text{-CaO}$ surface; a-clean surface, b) surface exposed to 4.5×10^4 L of SO_2 .

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DRY SORBENT RECYCLE PROCESSES

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ABSTRACT

Previous work on once through dry sorbent injection processes indicated that the technology may be limited to moderate levels of SO_2 removal. Relatively low sorbent reactivity and high loading of solids into boiler convective sections are the primary limiting factors. SO_2 removal can be increased, and sorbent utilization improved significantly, while maintaining acceptable solids loading, by recycling the spent sorbent material. A dry sorbent recycle process model has been developed to examine SO_2 removal as a function of the recycle ratio. Factors such as the effectiveness of the recycled sorbent material, furnace sorbent/ash particulate loading, and sorbent/ash separation are taken into account. Laboratory tests of a continuous recycle system have been used to examine SO_2 removal levels, recycle ratios, and recycle effectiveness factors for several sorbents. Possible commercial applications of the dry sorbent recycle process are discussed.

INTRODUCTION

Many investigators have been working to develop dry sorbent injection processes for the control of sulfur dioxide (SO_2) emissions for fossil fuel-fired boilers. (1,2) These processes have generally been developed for retrofit "acid rain" control, where low capital cost and modest levels of SO_2 removal (typically 50% to 70%) are the primary development targets. (3) The principal focus of recent research programs has been on producing "super sorbents" for use in once through configurations. (4) These highly reactive materials are

expected to achieve the necessary levels of SO_2 removal while requiring less reagent.

A much smaller effort has been directed towards developing calcium-based dry sorbent processes for plants using low sulfur coals. Previous efforts by this project team demonstrated that calcium-based sorbents became slightly less effective as flue gas SO_2 levels decrease.(5) However, the previous study also pointed out that much less sorbent, on a mass basis, was required for the same calcium to sulfur mole ratio (Ca/S ratio) when compared to a high sulfur coal system. This suggests that higher calcium to sulfur ratios are possible for low sulfur dry sorbent processes before economic constraints or solid particle loading limits are reached.

Table 1 presents a theoretical example which illustrates the potential for lower sorbent mass loading in low sulfur systems. The table compares sorbent mass requirements for hypothetical coals with 3% sulfur (typical Eastern) and 0.5% sulfur (low sulfur Western). Both coals are assumed to have 10% ash content and identical heating values. For this simple case, and given that all other factors are equal, a dry SO_2 process for a coal with one sixth the sulfur content can use a calcium to sulfur molar ratio six times higher without increasing solids loadings beyond acceptable levels.

HIGH CALCIUM TO SULFUR RATIO "ONCE THROUGH" TESTS

In order to investigate the potential for using higher calcium to sulfur ratios in low sulfur coal applications, a series of laboratory tests were conducted to examine SO_2 removal levels in a once through configuration at high Ca/S ratios. Commercially available sorbents were tested under simulated (gas-fired, SO_2 added) low sulfur coal test conditions. Figure 1 shows typical results from two of these tests. Ninety percent SO_2 removal was obtained at calcium to sulfur mole ratios of 6 and 26 for commercial dolomitic monohydrate and limestone, respectively. A Ca/S ratio of 6 may seem high, but the required mass of sorbent, and therefore, the sorbent solids loading, is roughly comparable to a Ca/S ratio of one for a high sulfur coal application.

While high Ca/S ratios may be technically feasible for high levels of SO_2 control, such high sorbent feed rates may pose other problems, even for low sulfur applications. There are four primary factors which place practical limitations on the amount of fresh sorbent which can be injected: waste disposal volume, particulate mass loading, boiler efficiency decreases, and process cost. As sorbent feed rates are increased, large volumes of partially reacted, spent sorbent are generated and must be disposed of safely. Solid particle loading constraints in the furnace convective sections and downstream particulate collection equipment also place practical limits on the amount of sorbent which can be injected. Additionally, as very large amounts of sorbent are added, boiler efficiency decreases as available heat is used to calcine, or dehydrate the sorbent materials. And finally, dry sorbent processes become expensive compared to other alternatives when high sorbent feed rates are required.

THE RECYCLE CONCEPT

In light of the limiting factors discussed above, modifications to the dry sorbent process are needed in order to reduce the initial sorbent feed requirements and utilize the material more completely. Recycling the partially

reacted, spent sorbent is one promising alternative which overcomes many of these limitations.

Recycle is not a new concept, and is commonly used in process industries to improve product yield and reagent utilization. Spent sorbent recycle has been examined briefly by other researchers for high sulfur coal applications;(6,7,8) however, based on furnace ash loading considerations, recycle can be more easily applied to low sulfur coal systems, where sorbent mass requirements are intrinsically lower. There may also be site specific situations where recycle can be applied advantageously to high sulfur processes.

Figure 2 shows the basic block diagram of a sorbent recycle system; Figure 3 shows how the basic recycle concept might be implemented in a power plant. Sorbent (any type) is injected into the boiler, at the proper temperature, where the sorbent reacts to capture SO_2 . The partially reacted sorbent material is collected in a particulate control device, typically a precipitator or a fabric filter. Because the sorbent is only partially sulfated, the unreacted portion of the calcium present in the spent material should be available to react further and capture more SO_2 .

RECYCLED SORBENT REACTIVITY TESTS

It was not known how effectively spent sorbents would capture SO_2 , so a series of preliminary, "proof of concept" laboratory tests were conducted to find out. Tests were carried out by injecting fresh sorbent into a once through, gas-fired combustor, collecting the partially sulfated material, and re-injecting the material to capture more SO_2 . This cycle was then repeated a number of times. The Ca/S ratio for the recycled sorbent was determined based on the unreacted or "available" calcium in the sorbent. In other words, calcium which was utilized in previous recycle passes was subtracted from the total reagent calcium to arrive at the Ca/S ratios reported for the experiments.

Figure 4 shows the results of one set of tests for a commercial dolomite. As can be seen, initially the recycled sorbent was quite reactive; however, the reactivity decreases as sulfation of the material proceeds. After seven passes through the combustor, the partially utilized sorbent was still about 74% as effective at removing SO_2 as the fresh sorbent.

From a physical point of view, this decrease in reactivity might be explained by sorbent particle pore plugging or the build up of a calcium sulfate shell around the particle, thereby limiting access to additional reactive calcium sites on the particle. Further testing has shown that spent sorbent can be re-injected and recycled to a point where it will no longer react effectively; however, complete utilization of the sorbent has not been achieved.

RECYCLE ANALYSIS

There are two primary elements which control the level of SO_2 removal in a recycle system: the amount of fresh feed and the amount of recycled material. From a practical point of view, it is desirable to keep the fresh sorbent rate low to improve process economics, and to keep the recycle feed rate low to avoid solids overloading in the boiler and particulate control systems. However, recycle and fresh feed are interconnected: if the fresh feed is decreased, the recycle rate must be increased (to maintain the same level of

SO₂ removal). The relationship between recycled and fresh material must be determined in order to predict SO₂ removal for the recycle process.

This trade off between recycle and fresh material is expressed as the recycle ratio. It is defined as:

$$\text{recycle ratio (R)} = \frac{\text{moles calcium in recycle}}{\text{moles calcium in fresh sorbent}}$$

The mass recycle ratio, R_m , is defined similarly:

$$\text{mass recycle ratio (R}_m\text{)} = \frac{\text{total mass of recycle}}{\text{total mass of fresh sorbent}}$$

It is important to remember that only a portion of the recycled sorbent is available for further reaction. Part of the material has already been sulfated and is "unavailable". Ca/S ratios in the recycle system are calculated based on the available calcium; the previously utilized material is not available for further reaction and is, therefore, not counted.

The mass of recycled material in the boiler at any time consists of a distribution of sorbent that has passed through the boiler, or been recycled anywhere from one to almost an infinite number of times. The fraction of calcium (molar basis) f_i , which has passed through the boiler i times, is a function of the recycle ratio:

$$f_i = \frac{R^i}{(1+R)^{i+1}}$$

As was shown in Figure 4, each sorbent pass has a different reactivity, depending on how many times it has been recycled. Based on Figure 4, the SO₂ capture for each fraction of sorbent can be summed to calculate the overall SO₂ removal for the recycle process. However, in practice this approach presents difficulties, because "batch" recycle tests are quite time consuming.

THE RECYCLE EFFECTIVENESS FACTOR

The decreased effectiveness of the recycled sorbent can be handled in a much simpler fashion by introducing an "effectiveness factor" into the recycle calculations. The effectiveness factor is defined as:

$$\text{effectiveness factor (D)} = \frac{\text{SO}_2 \text{ removal recycle material}}{\text{SO}_2 \text{ removal fresh material}}$$

where the available calcium to sulfur mole ratios for both materials are equal.

The effectiveness factor is not a fundamental, intrinsic property of the sorbent, but rather a convenient ratio used to simplify recycle calculations. It can be determined experimentally for each sorbent type, calcium to sulfur ratio, recycle ratio, injection temperature, particle size, and overall level of sorbent utilization. In other words, it is a function of the sorbent and the process, and therefore must be derived from experiment rather than from physical principles.

The relationship of the effectiveness factor to the recycle ratio can be shown quite easily. If D_i is the effectiveness for the sorbent fraction f_i (fraction which has passed through the boiler i times), then the overall effectiveness for the recycle stream is given by the equation:

$$D = (f_1 * D_1) + (f_2 * D_2) + (f_3 * D_3) + \dots + (f_i * D_i)$$

Since f_i is related to the recycle ratio (see above), D is also a function of the recycle ratio. Figure 5 shows a theoretical plot of the required recycle ratio as a function of the effectiveness factor for a fixed level of SO_2 removal, and at various fresh sorbent feed ratios. It is important to note that for lower feed Ca/S ratios (one of the primary goals of recycling), changes in the effectiveness factor have a significant impact on the required recycle rate (to maintain the same level of SO_2 removal).

Likewise, temperature will also affect the recycle process. While most once through processes may benefit from relatively high injection temperatures (2000 to 2200°F), continuous exposure of recycled material to high temperatures may result in sintering and decreased effectiveness. Thus recycle processes will likely utilize somewhat lower injection temperatures, typically 1600 to 1800°F.

The use of an effectiveness factor has not been reported by other researchers and represents a unique approach to this analysis. (6,7) Previous calculations of sorbent recycle systems have shown results which appear optimistic because decreases in recycled sorbent performance was not taken into account. (6)

EFFECTIVE CALCIUM TO SULFUR RATIO

SO_2 removal in the recycle process is the sum of the SO_2 removed by the fresh sorbent and the SO_2 removed by the effective recycled sorbent. The effective calcium to sulfur mole ratio, Ca/S(eff), is defined (on a molar basis) as:

$$Ca/S(eff) = \frac{Ca \text{ (feed)} + [D * Ca(\text{available in recycle})]}{\text{Sulfur in}}$$

Note that "available calcium" refers to the unreacted calcium in the recycle stream. And, of the available calcium, only D percent (the effectiveness factor) will react to further capture SO_2 .

The above definitions simplify the calculation of SO_2 removal in recycle systems. Ca/S(eff) represents the calcium to sulfur ratio of combined fresh and recycled material which is "just as reactive" as fresh sorbent. SO_2 removal is, therefore, directly related to Ca/S(eff). In fact, SO_2 removal can be read directly from fresh sorbent Ca/S versus SO_2 removal curves, because the effective calcium in the combined feed and recycle streams is just as good as fresh sorbent.

RECYCLE MODEL

In order to calculate SO_2 removals for the recycle system, a simple computer model was developed which implements the recycle mathematics for a variety of sorbents and process configurations. The most important input variables are fresh sorbent type and feed rate, Ca/S(eff), and the recycle effectiveness factor. Fuel type, sulfur, and ash content, sorbent performance curves (SO_2 removal vs. Ca/S(eff)), and sorbent/ash separation parameters can also be

entered. Calculated results include percent SO₂ removal, recycle rates and ratios, and boiler solids loading. The model has been developed on a computer spreadsheet so that it is easy to conduct parametric and sensitivity studies of the recycle process.

SAMPLE CALCULATIONS

The recycle model is most readily demonstrated with some simple examples using the generic recycle system shown in Figure 3. These sample calculations, which are based on laboratory sorbent performance data at low sulfur conditions, utilize a hypothetical coal with 0.6% sulfur, 10% ash, and a 12,000 Btu/lb heating value. The sorbent is a commercial dolomitic monohydrate (atmospheric hydrated dolomitic lime or "hydrate" for short); the Ca/S fresh feed mole ratio is 2. If this sorbent was injected in a once through configuration (without recycle), about 48% SO₂ removal would be expected at this Ca/S feed ratio.

Table 2 shows the comparison of a once through process to a recycle process incorporating a modest level of recycle. Ash has not been included in these calculations and will be addressed later. A recycle ratio of four increases the SO₂ removal from 48% (once through) to 76% (recycle). Also of importance, the sorbent utilization increases from 24% to 38% when recycle is used.

Table 3 continues the example in Table 2 by examining the impact of ash on the recycle process. Both cases in Table 3 are based on a 10% ash coal. The first case assumes that no ash separation takes place. In other words, the combined ash and spent sorbent stream is collected directly from the particulate collection device and re-injected into the furnace with no intermediate processing. SO₂ removal is unchanged for the previous example; however, the total sorbent and ash loading is quite high. The second case incorporates a sorbent/ash separation step which preferentially removes 50% of the fly ash from the recycle stream and allows the recycle stream to be enriched in sorbent. With 50% ash removal, the furnace solids loading is reduced to more acceptable levels. Fly ash separation processes are discussed in a later section.

CONTINUOUS RECYCLE TESTING

In order to verify the model assumptions and determine effectiveness factors for various sorbents and process configurations, a series of recycle tests were conducted in a pilot scale combustion system designed to operate in the continuous recycle mode. As discussed previously, effectiveness factors can also be calculated from batch (once through) experiments, but these tests proved to be time consuming and costly; continuous recycle tests were much easier to perform.

Tests were conducted in a new combustor developed for this program. The combustor is a vertical, down-fired unit which burns natural gas with SO₂ added. The reactor has a 12 inch diameter test section which is 5 feet long; the test section is lined with 310 stainless steel to reduce the possibility of sorbent deposits on the reactor walls. The burner is typically fired at 250,000 Btu/hr which gives the combustor a 1.2 second residence time at the typical 1650°F injection temperature. The total temperature drop through the reactor is about 150°F. Once through sorbent performance verification tests in the new reactor compared favorably with previous test results from other combustor systems.

Fresh sorbent and recycled material are fed to the reactor by separate loss of weight (gravimetric) feeders into a common injection line. Injectors are located below the burner level and consist of two 1/2 inch diametrically opposed injectors using air for sorbent transport. Solids exiting the combustor are rapidly quenched with dilution air, then collected in a small pulse jet baghouse. Other systems, such as sampling, cooling, and gas analysis are the same as reported previously. (5) A diagram of the continuous recycle test system is shown in Figure 6.

CONTINUOUS RECYCLE TEST RESULTS

Tests were conducted by setting both gravimetric feeders to preset specified feed rates, and then allowing the system to run long enough to come to steady state. Spent sorbent was collected from the baghouse hoppers hourly and manually transferred and mixed into the recycle feeder. Using this procedure, the reactor would require 30 to 50 hours of continuous run time to reach equilibrium. Figure 7 shows an SO₂ removal versus time plot for a typical experiment.

Once steady state was achieved, the effectiveness factor for the combination of sorbent and process conditions was determined from the following experimental data: the overall SO₂ removal at steady state, the fresh sorbent Ca/S ratio, the recycle ratio (determined from measured gravimetric feed rates), and Ca/S(eff).

Table 4 shows the results from two recycle experiments. Both tests were conducted at simulated low sulfur flue gas conditions, without ash, using hydrated dolomitic material. In the first experiment, 70% SO₂ removal was obtained at a fresh feed Ca/S ratio of 1.5 and a mass recycle ratio of 8. The measured sorbent utilization of 46% was higher than typically obtained in once through dry sorbent process under low sulfur conditions. Figure 7 shows the time history plot for this test. Seventy percent SO₂ removal was achieved for over sixty hours once the system reached steady state.

The second test shown in Table 4 achieved 79% SO₂ removal. About sixty hours of continuous operating time were required to reach steady state. The final steady state fresh feed Ca/S ratio was 2.5, and the mass recycle ratio was 1.9. The measured sorbent utilization was 31% which was lower than the previous test, and probably lower than desired for a commercial application.

The experimental recycle effectiveness factor was higher in the second test than the first test. The difference in recycle effectiveness between these two tests again illustrates the earlier comments that the effectiveness factor is a function of the overall process conditions (ie. recycle ratio, fresh Ca/S ratio) as well as the type of sorbent.

KEY ISSUES FOR FUTURE RECYCLE APPLICATIONS

A number of key issues for recycle processes are currently unresolved. Perhaps the principal issue which must be addressed is that of potential high particulate loading in the boiler. Allowable boiler solids mass loading depends upon various plant specific factors. Some plants, which were designed for high ash fuels (eg. with wide convective bank tube spacing, sufficient particulate collection equipment, or extra sootblowing capacity), may have a greater tolerance for the increased solids loading typical in recycle processes.

Another way to deal with this issue is to use recycle schemes which separate the ash and sorbent. Preliminary engineering evaluations have identified commercially available techniques to separate fly ash and sorbent using particle size classification. Cyclones and multiclones appear viable for removing larger particle sorbents, while air classification systems may be feasible for smaller sorbent particles.

Another key issue is spent sorbent waste disposal. Recycle systems inherently produce less waste than once through injection systems because the sorbent is more highly utilized in the recycle process. Preliminary waste disposal tests of combined recycle waste and fly ash have indicated that recycle wastes have good "cementitious" properties. The waste is, however, quite reactive when it is contacted with water (due to the free lime present) and may require special handling. This problem is common to most dry sorbent and fluidized bed combustor wastes.(9)

Recycle may be well suited for low sulfur coal applications where sorbent mass loadings are low. However, several potential high sulfur applications have also been identified. Use of a high recycle ratio limestone sorbent process in pulverized coal boilers (similar to a circulating fluidized bed) was recently suggested by two researchers.(6,10) Recycle may also be attractive for boilers which use cleaned coal with a substantially lower ash content. These, and other potential applications will have to be evaluated on a case by case basis. Recycle applicability will depend on the fuel sulfur and ash levels, the level of SO₂ control required, and available sorbent type. Costs for recycle systems have not yet been fully evaluated, but are expected to be in the range of other dry sorbent processes.

CONCLUSIONS

The use of recycle in dry sorbent injection SO₂ control systems appears to be a promising method to improve process performance. The level of SO₂ removal and the overall sorbent utilization can be improved, while reducing sorbent feed rates, using recycle techniques. Design of the recycle process involves evaluating the trade off between fresh sorbent feed and recycle feed. Sorbent recycle processes appear well suited for use with low sulfur and low ash fuels, but may also provide process performance enhancement for site specific high sulfur or retrofit applications. Key areas which require further process development include experimental evaluation of recycle effectiveness factors, development of sorbent/ash separation processes, and development of system designs and costs.

It is also important to note that, while recycle concepts look promising on paper, in the lab, and at the pilot scale, large scale test work has not yet been conducted. Demonstration or larger scale testing of sorbent recycle processes will be necessary if this technology is to become widely accepted.

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FIGURE 1
SO₂ Removal With Common Sorbents
At High Calcium to Sulfur Ratios

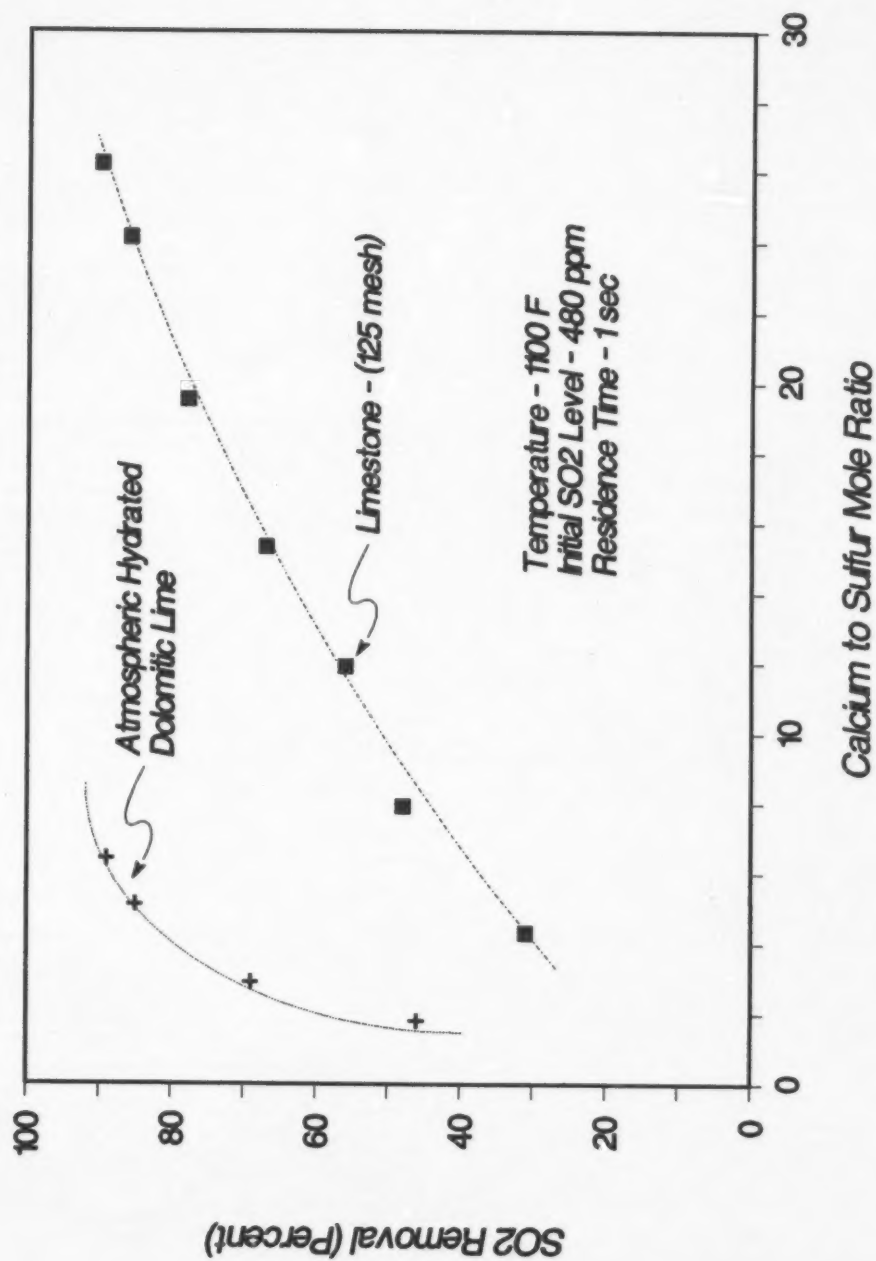


FIGURE 2

Generic Dry Sorbent Recycle Process

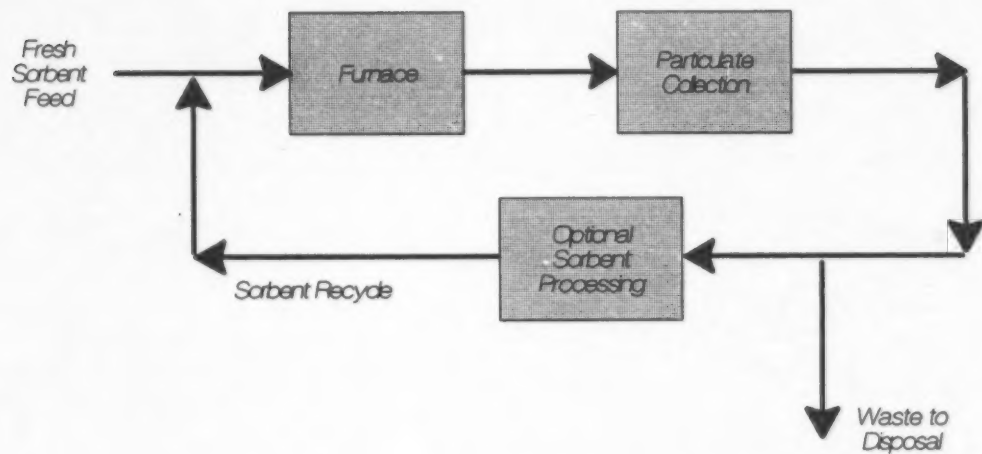


FIGURE 3

Typical Dry Sorbent Recycle Process

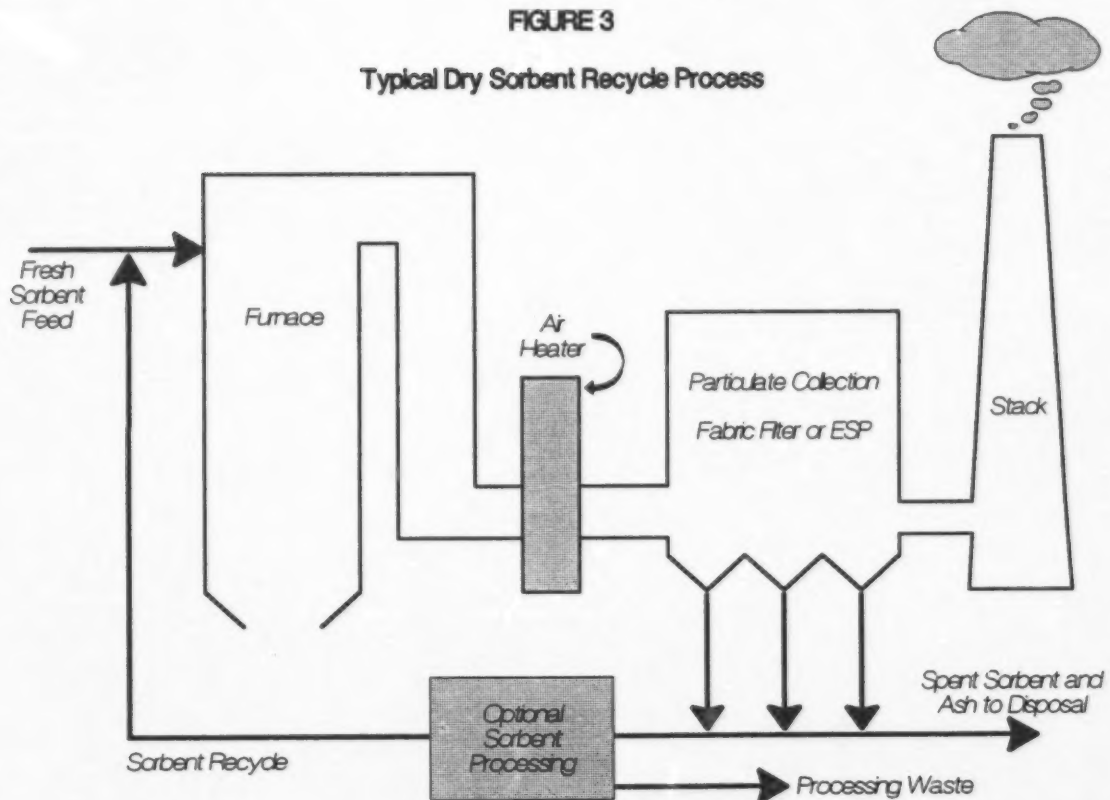


FIGURE 4
Lower Effectiveness For Recycled Sorbent

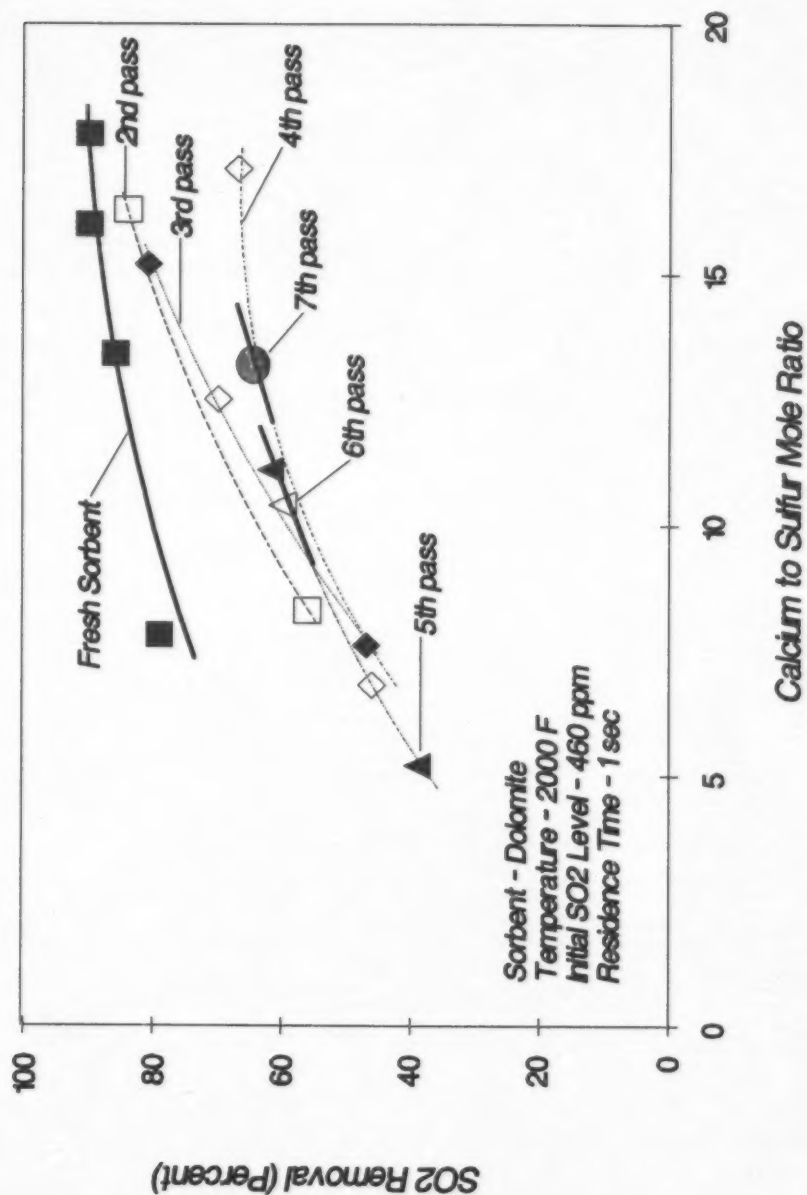


FIGURE 5

Impact of Effectiveness Factor on Recycle Ratio

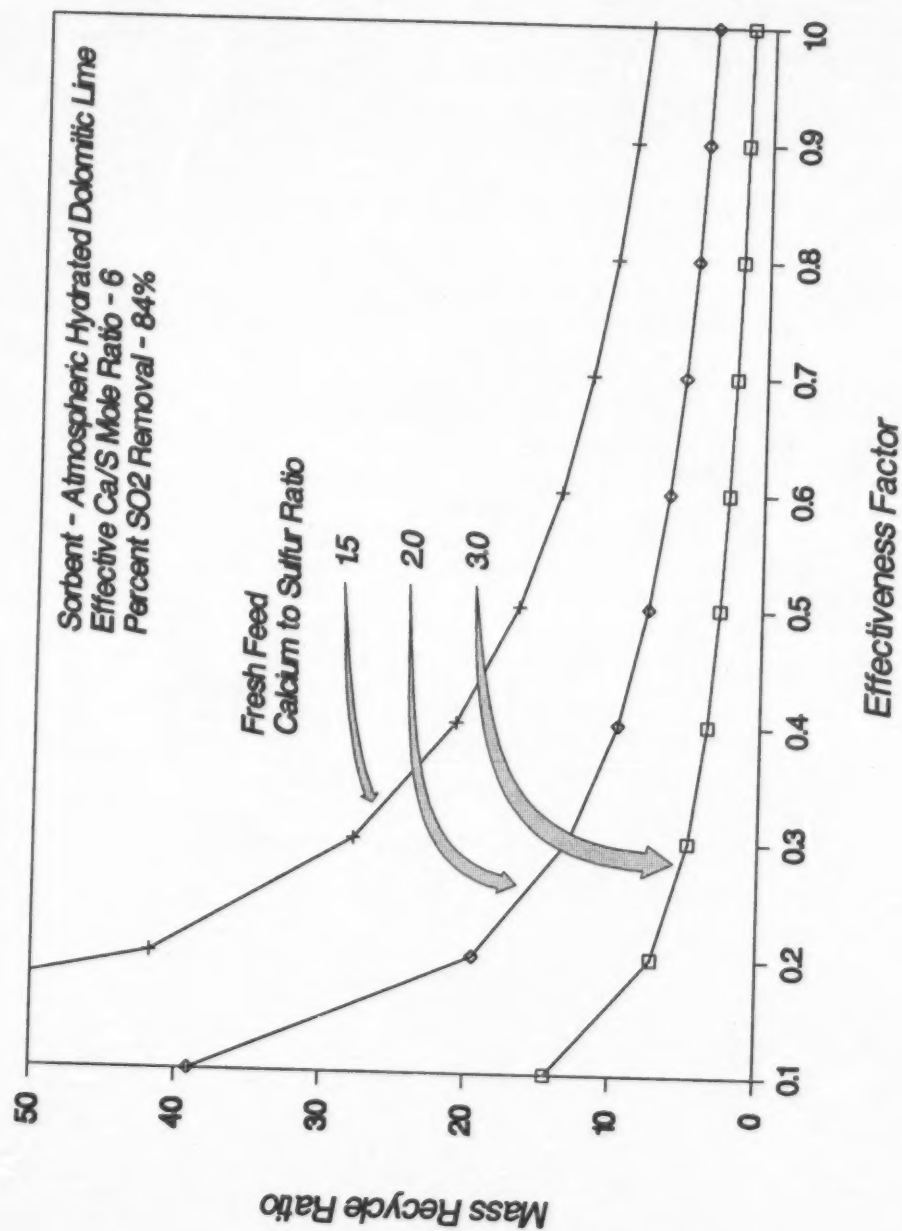


FIGURE 6
Continuous Recycle Pilot Facility

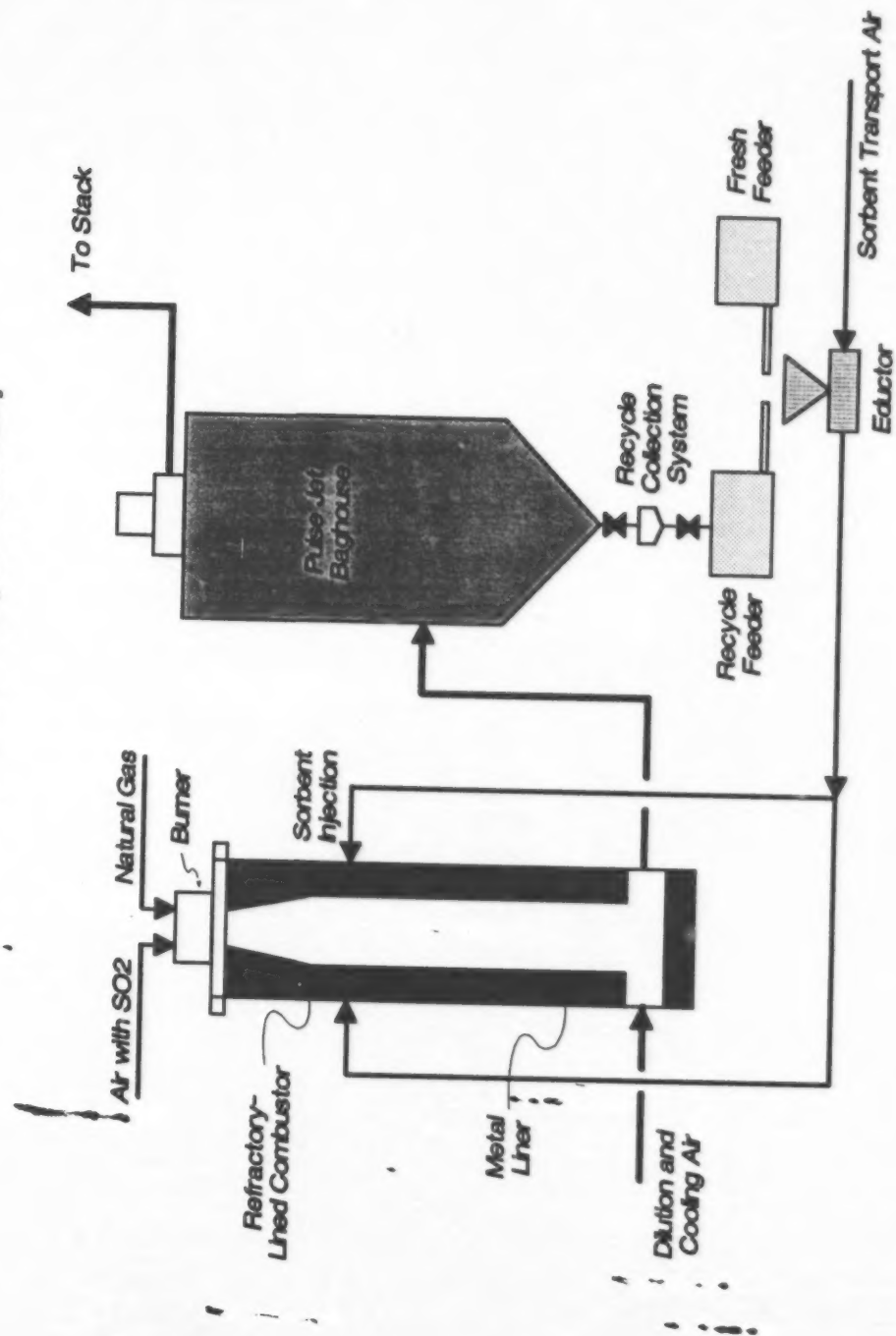


FIGURE 7
Continuous Recycle Laboratory Tests
Time Required to Reach Steady State
 (See Test Data in Table 4)

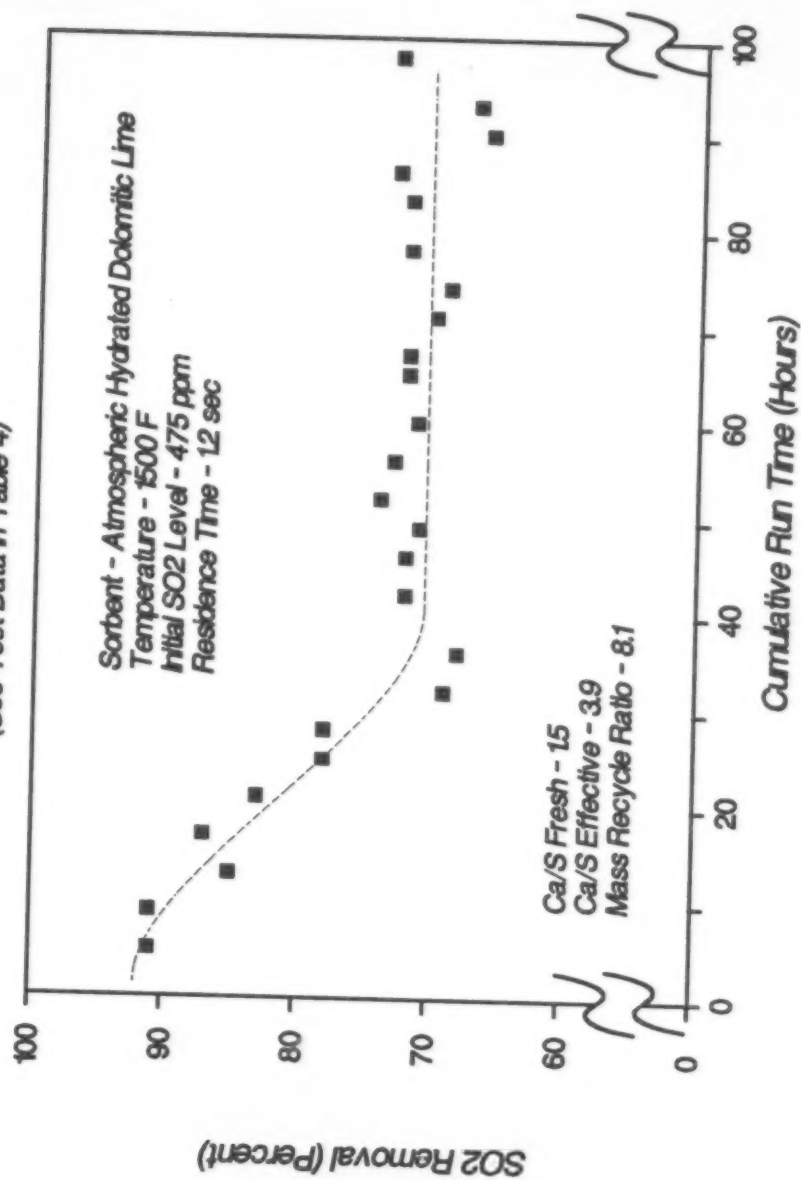


TABLE 1
ONCE THROUGH DRY SORBENT INJECTION PROCESS
HYPOTHETICAL COMPARISON OF MASS LOADING
HIGH SULFUR VS. LOW SULFUR COAL

BASIS: Calcium Oxide Sorbent
 10% Ash Coal

Fuel Sulfur (percent)	Fuel (lbs)	Ca/S Mole ratio	Sorbent (lbs)	Ash (lbs)
3%	100	2	10.5	10
0.5%	100	2	1.8	10
0.5%	100	12	10.5	10

TABLE 2
COMPARISON OF
ONCE THROUGH AND RECYCLE PROCESSES

BASIS: Coal - 12000 Btu/lb, 0.6% sulfur
 Sorbent - Atmospheric Hydrated Dolomitic Lime

	ONCE THROUGH PROCESS	RECYCLE PROCESS
Ca/S - Fresh Feed	2	2
Ca/S - Effective	2	5
Effectiveness Factor	NA	0.65
SO ₂ Removal (%)	48	76
Sorbent Utilization (%)	24	38
Mass Recycle Ratio	0	4

TABLE 3
COMPARISON OF RECYCLE WITH AND WITHOUT ASH SEPARATION

BASIS: Coal - 12000 Btu/lb, 0.6% sulfur
Sorbent - Atmospheric Hydrated Dolomitic Lime
Coal Ash - 10% Fly Ash - 85% of Coal Ash

	RECYCLE NO ASH REMOVED	RECYCLE 50% ASH REMOVED*
Ca/S - Fresh Feed	2	2
Ca/S - Effective	5	5
Effectiveness Factor	0.65	0.65
SO ₂ Removal (%)	76	76
Sorbent Utilization (%)	38	38
Mass Recycle Ratio	11	5
Sorbent/Ash Mass Loading --		
lbs/MMBTU Fuel Basis [#]	54	31
(Sorbent+Ash)/Ash Basis [@]	7.6	4.4

* 50% of ash in recycled stream is removed before stream is re-injected into the boiler

[#] lbs of recycled stream divided by the fuel heat input

[@] lbs of recycled stream divided by original fly ash mass

TABLE 4
CONTINUOUS LABORATORY RECYCLE TEST RESULTS

TEST CONDITIONS

Sorbent	Hydrated Dolomitic Lime
Temperature	1500°F
Initial SO ₂ level	475 ppm
Residence time	1.2 seconds

RESULTS	TEST 1	TEST 2
Ca/S - Fresh Feed	1.5	2.5
Ca/S - Effective	3.9	4.6
Effectiveness Factor	0.4	0.67
SO ₂ Removal (%)	70%	79%
Sorbent Utilization (%)	46%	31%
Mass Recycle Ratio	8.1	1.9

CALCIUM HYDROXIDE SORBENT REACTIVITY WITH SULFUR DIOXIDE
FROM X-RAY DIFFRACTION PEAK PROFILES

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ABSTRACT

It was observed early in the history of x-ray diffraction (XRD) analysis that the spectral peaks were not discrete lines as the Bragg equation would predict for a perfect crystal lattice. Instead, the intensities decrease gradually from the maximum at the Bragg angle. XRD line broadening comes about from decreasing crystallite (grain) size, increasing crystal lattice distortion, and instrument effects.

It is apparent that crystallite size can affect gas-solid reactions by modifying the interface between the two phases. It is further proposed that crystal lattice strain could contribute to reactivity by decreasing the stability of the solid and providing a source of activation energy from the strain energy stored in the lattice. This presentation will show the results of the XRD micro-structure analysis on LIMB sorbent materials.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation.

INTRODUCTION

The Air and Energy Engineering Research Laboratory of the Environmental Protection Agency (EPA) is currently investigating the injection of dry calcium hydroxide [$\text{Ca}(\text{OH})_2$] into coal fired power plant combustion streams for the removal of sulfur dioxide (SO_2). The efficiency of the $\text{Ca}(\text{OH})_2$ sorbent material can vary over a considerable range depending on a number of factors. The $\text{Ca}(\text{OH})_2$ is produced by heating the raw mineral calcium carbonate (CaCO_3) to drive off carbon dioxide (CO_2) to form calcium oxide (CaO). The oxide is then slaked with water to form the $\text{Ca}(\text{OH})_2$. The efficiency of the $\text{Ca}(\text{OH})_2$ for SO_2 removal can be affected by the raw mineral composition and structure. It can also be affected by the time, temperature, and pressure used in the slaking process. It has further been shown that the introduction of certain agents, particularly lignosite, during slaking, can greatly improve the efficiency (1). Because of the many factors affecting the efficiency and because of the importance of achieving the best efficiency, it is of utmost importance to be able to reliably characterize the sorbents produced from different raw minerals by different processes. It is economically infeasible to test all of the candidate sorbents in a full scale furnace. At present, bench-scale furnace testing is the only method acceptable for evaluation. This severely limits the extent of testing available because of the level of time and resources necessary for bench scale tests. There is a critical need for a routine evaluation test so that more different sorbent materials can be tested. Furthermore, even after a particular sorbent is chosen it will be necessary to have a reliable test for quality control. A number of laboratory tests have been used for the evaluation of sorbents. These include microscopic mineralogical observation; Brunauer, Emmett, and Teller (B.E.T.) surface measurements; thermogravimetric analysis; and differential scanning calorimetry (2). None of these, so far, have been able to give reliable comparison criteria. This problem has led to an attempt to utilize x-ray diffraction for the evaluation.

THEORY

X-ray powder diffraction (XRD) is, today, the most powerful technique available for the identification of chemical compounds or phases present in solid materials. XRD is possible because of the geometric order of solids. The degree of order can vary from almost nothing, as in glasses, to very high order in materials such as quartz. It should be mentioned that some order is present in all solids. Even such amorphous materials as glass, rubber, and petroleum jelly do exhibit some order which is manifested as XRD spectra with a few very broad peaks. On the other hand, highly ordered or crystalline substances yield XRD spectra of many sharp peaks. Most solids do show sufficient XRD spectra to enable their identification by comparison to standard recorded spectral files. An organization known as the Joint Committee for Powder Diffraction Spectra (JCPDS) has spectral files on over 40,000 phases which are updated yearly. The data sets are available on a 3 x 5 in. (8 x 13 cm) card for each phase or card images bound in book form or on magnetic media organized for computer searches. These data or privately generated data sets can be compared against XRD spectra of unknowns to determine the phases present. Unknowns consisting of pure phases or mixtures can be identified by executing systematic searches against the data base by manual methods or with computer assistance. As a general rule, the limit of detection for individual components of a mixture is about 5%.

The XRD spectra, as mentioned earlier, arise from the order within a solid material. If one considers a simple compound such as table salt it can be assumed to have an arrangement of alternating sodium and chlorine ions with each of the ions surrounded by six of the other species equally spaced and all at 90° to each other. The pattern is repeated throughout the salt crystal. It is seen that many families of planes can be drawn through the crystal lattice which intersect the atoms at regular intervals. Each of the families of planes will be spaced at a regular distance from each other. From the angle of reflection θ , of an x-ray beam, with wavelength λ (1.54056 for copper K α 1 radiation), one can determine the spacing between the planes d , from the Bragg equation:

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is the order of the reflection. The angle θ is known as the Bragg angle. Because of the variation in the size, mass, orbital, and electrostatic properties of atoms, ions, molecules, and radicals which make up crystals, the possible number of XRD spectra is almost infinite. The standard XRD data sets consist of a list of d values and intensity values (I) for each compound or phase.

If a crystalline material were perfect and every respective distance d , for each family of planes in the material, were precisely repeated (and if the x-ray measuring device were perfect), all of the x-ray intensity would, for each given d space, be reflected only at the respective Bragg angle θ . However, no crystalline material is perfect (true also for x-ray measuring devices) and, consequently, the reflected x-ray intensity for the d value does not all occur as an infinitesimally narrow line but is distributed in a pattern with maximum intensity at the Bragg angle and decreasing in both directions going away from the Bragg angle.

Crystalline materials can be imperfect in a number of ways. Most solid materials are not one single contiguous crystal lattice, but are composed of agglomerations of many small crystallites. The crystallite is the largest uninterrupted crystal unit. When crystallites are smaller than 1000 Å, the width of diffraction peaks starts to increase. This enables a measurement of crystallite dimensions down to a limit where they approach the dimensions of the x-ray radiation.

Another type of imperfection which can occur in a crystal is distortion. Distortion is caused by significant variations in the d spacing. This can happen when an alien species is introduced into the crystal lattice; e.g., potassium impurity in sodium chloride. It can also come about from other than ideal crystallization conditions such as rapid temperature change or the presence of surface active agents. Other types of distortions can occur from slippage of crystal planes which takes place during cold working of ductile materials, such as metals.

It has been described how the profile of the XRD peak is affected by three factors: the instrument effects, the crystallite size, and the distortion within the crystal lattice. The first attempt to relate peak shape to crystallite size was by Scherrer (3), who derived the following expression for the peak half width

$$B(2\theta) = 0.94 \lambda / L \cos \theta \quad (2)$$

with B , in radians, as a function of the radiation wavelength, the crystallite dimension L , in Å, and the Bragg angle.

The Scherrer equation assumes that all peak broadening is due to small crystallite size and does not consider distortion effects. Instrument broadening is not considered in a rigorous manner but instrument effects may be accounted for by subtracting the half width for a standard material which has very large, perfect crystals and very little distortion.

It has been postulated that peak broadening due to small crystallite size is of the Cauchy or Lorentzian form

$$y = \frac{I_0}{1 + kx^2} \quad (3)$$

while peak broadening due to lattice distortion is of the Gaussian form (4)

$$y = I_0 e^{-kx^2} \quad (4)$$

Several techniques for separation of size and strain effects attempt to utilize this property (5). These methods have an advantage in needing XRD data for only one peak but are limited in the amount of information given and theoretical rigor.

The most powerful method for separation of size and strain effects available, at present, is that originally proposed by Warren and Averbach (6, 7, 8). According to Warren the distribution of diffracted power can be expressed as a Fourier series:

$$P(2\theta) = K(\theta) \cdot N \cdot \sum_{n=-\infty}^{\infty} (A_n \cos 2\pi n h_3 + B_n \sin 2\pi n h_3) \quad (5)$$

with the Fourier coefficients for the expression given as:

$$A_n = \frac{N_n}{N_3} \langle \cos 2\pi n Z_n \rangle, \text{ and} \quad (6a)$$

$$B_n = \frac{-N_n}{N_3} \langle \sin 2\pi n Z_n \rangle \quad (6b)$$

In order to gain an understanding of the meaning of the parameters, it is helpful to consider a sample crystallite with the structure shown in Fig. 1. The sample crystallite is composed of columns of surrogate cells to be measured in units of a'_3 which is not related to the crystal unit cell or the crystallite dimensions. This unit of measurement comes from the peak width and the wavelength of the measuring radiation. The diffraction peak is shown in Fig. 2. The angle θ_0 is the angle where maximum intensity occurs and θ_1 and θ_2 represent the angles where the intensity approaches zero. The unit for column measurement a'_3 is then:

$$a'_3 = \frac{\lambda}{4(\sin \theta_2 - \sin \theta_0)} \quad (7)$$

The sample crystallite (Fig. 1) has a total cell number $N_3 = 35$. The 35 cells are arranged in 11 columns. The x-ray reflections come only from pairs of cells perpendicular to the reflecting planes. Each of the columns is made up of all combinations of pairs of cells from 0 to $n-1$ cell units apart where n is the number of cell units in the column. The average column length is $L_{avg} = 35/11 = 3.18$.

If only symmetrical contributions to peak broadening are considered, then only the cosine terms of the peak profile function need to be considered. The cosine coefficient given in Eq. 6 consists of two components. The one quantity, N_n/N_3 , depends only on column length. It is a size coefficient and is represented by $A_n^S = N_n/N_3$. The second quantity is represented by $\cos 2\pi \ell Z_n$. The cosine coefficient obtained from experiment is the product of the size and distortion coefficients:

$$A_n = A_n^S A_n^D \quad (8)$$

The expression for the general Fourier coefficient is now:

$$A_n = \frac{N_n}{N_3} (\cos 2\pi \ell Z_n) \quad (9)$$

Before the size and strain effects can be separated the instrument effects must be removed. To do this it is first necessary to remove the asymmetry of the experimental XRD peak which is caused by the $K\alpha_2$ peak contribution to the larger $K\alpha_1$ peak. This is accomplished by the Rachinger correction proposed by DuMond (9), for another reason. Fourier coefficients are then derived to fit the corrected experimental data. According to Stokes (10), the instrument effects on line broadening can be removed by dividing the Fourier coefficients of the sample XRD peak by those of a standard material which has relatively minimal line broadening from size or strain. Finally, a set of Fourier coefficients are available which contain only size and strain effects.

Warren and Averbach (6) proposed the following method for size and strain effect separations. In Eq. 9, it is seen that distortion coefficient A_n^D is dependent on order ℓ while the size coefficient is independent of order. The separation process is simplified by making the assumption that the values of ℓ and n will be small so that the product ℓZ_n is small, the cos can be expanded $\langle \cos 2\pi \ell Z_n \rangle \rightarrow 1 - 2\pi^2 \ell^2 \langle Z_n^2 \rangle$ and taking the logarithm yields

$$\ln \langle \cos 2\pi \ell Z_n \rangle = \ln (1 - 2\pi^2 \ell^2 \langle Z_n^2 \rangle) = -2\pi^2 \ell^2 \langle Z_n^2 \rangle \quad (10)$$

therefore:

$$\ln A_n(\ell) = \ln A_n^S - 2\pi^2 \langle Z_n^2 \rangle \ell^2, \quad (11)$$

$$y = b - m x$$

This expression is seen to be of the general slope-intercept form. If $\ln A_n(\ell)$ is plotted vs. ℓ^2 as shown in Fig. 3, it is seen that the intercepts of the ordinate yield the size coefficients and the slope contains the factor Z_n . The undistorted column length $L = na_3$ was described in Fig. 1. The quantity $\Delta L = Za_3$ represents the individual distorted cell lengths which make up the column. From the initial slopes of the lines in Fig. 3, the root mean square of the Z_n term is obtained. Strain ϵ is defined as the distorted distance divided by undistorted distance:

$$\epsilon_L = \frac{\Delta L}{L} \quad (12)$$

A typical plot of this function (strain, as a function of column length) that was produced by the program is shown in Fig. 4.

Using Eq. 7, and the fact that d is the lattice spacing, gives the expression:

$$I_n A_L(1/d) = I_n A_L^S - 2\pi^2 \langle \epsilon^2 \rangle L^2/d^2 \quad (13)$$

To interpret the size coefficient we refer to Fig. 1. The number of columns made up of N_n cells is:

$$N_n = \sum_{i=|n|}^{\infty} (i - |n|) p(i) \quad (14)$$

where $p(i)$ is the fraction of columns made up of i cells. The size coefficient A_n^S is then

$$A_n^S = \frac{N_n}{N_3} = \frac{1}{N_3} \sum_{i=|n|}^{\infty} (i - |n|) p(i) \quad (15)$$

This can be made into a smooth curve:

$$d A_n^S = -\frac{1}{N_3} \int_{i=|n|}^{\infty} p(i) di \quad (16)$$

A column length distribution then comes from differentiating the above equation to get

$$\frac{d^2 A_n^S}{d_n^2} = \frac{p(|n|)}{N_3} \quad (17)$$

A typical plot of this function produced by the program is shown in Fig. 5. The average particle size D can be obtained by plotting A_n^S versus N_3 as shown in Fig. 6.

EXPERIMENTAL

Six samples of sorbent and one of reagent Ca(OH)_2 were obtained for the first complete evaluation of the XRD method for estimating reactivity (11). Reactivity was evaluated in an isothermal flow reactor operating at 1000°C with 0.3% SO_2 and a 1 sec residence time.

The experimental data were taken on a Siemens model D-500 diffractometer. A copper x-ray tube was used running at 50 kV and 40 mA. A 1 degree entrance aperture and 0.05 degree receiving slit were used. A scintillation detector equipped with a graphite monochromator was used. The sample powders were packed in a side loading cell. The diffractometer was run and the data were processed with the Siemens DIFFRAC 500, version 1.1, operating system.

At the beginning of the study, a complete XRD scan was taken on a sample of the sorbent material. The phase was identified as JCPDS No. 4-733. The scan is shown in Fig. 7. Because of the relative high intensities and their isolation, the first (101) and second (202) order peaks seen at the two-theta angles of 34.1 and 76.8 degrees were chosen for the first Warren-Averbach analysis. Zinc oxide

(JCPDS No. 36-1451) was chosen as the standard, to account for instrument line broadening, because it had peaks close by (36.26 and 76.77 degrees) which were very narrow. The data were processed with the CRYSIZ program (12) which uses the Warren-Averbach technique. The program was written by Gerhard Zorn (12) of Siemens and is furnished as part of the Siemens DIFFRAC 500 operating system, version 1.1. Before running CRYSIZ, it is required that the experimental peak data be fitted to one of several functions available. The adoption of this step was an extremely important advance in the peak analysis because it smoothes out random noise and removes smaller interfering peaks. Without very smooth data it is not possible to get meaningful results according to Zorn (13) and Langford (14). A separate program generates the parameters for the functions to fit the data. As mentioned earlier, the XRD profiles contain components of Gaussian and Lorentzian functions. The type of function that was used for our data was the split Pearson VII function which allows flexibility in fitting complex peaks ranging from pure Gaussian to pure Lorentzian.

RESULTS AND DISCUSSION

The Warren-Averbach analysis provides much information about the microstructure. The major properties delineated are:

1. Average crystallite size (see Fig. 6).
2. Frequency of occurrence of column lengths as a function of column length (see Fig. 5 for an example), and the column length of maximum frequency of occurrence.
3. Half width of the frequency of occurrence column lengths as a function of column length.
4. Maximum determinable column length.
5. Strain at the average column length.
6. Strain as a function of column length (see Fig. 4 for an example).
7. Strain at the column length of maximum frequency of occurrence.
8. Strain at the column length of maximum determinable column length.

Some of the crystallite size data, along with the XRD peak half widths, are shown in Table 1 and some of the lattice strain data are given in Table 2. Both tables give the percent conversion data from the reactions of the Ca(OH)_2 sorbent samples with SO_2 described earlier. The percent conversion data is reported in units of moles of Ca reacted divided by moles of Ca available times 100. The samples labeled "Lig." were processed with the respective percentages of lignosite, a by-product of the paper industry.

The percent conversion was plotted vs. the XRD data in the two tables to determine if relationships existed. The average column lengths are plotted in Fig. 8, and the maximum determinable column lengths are plotted in Fig. 9. The average column length is something like the average cross section dimension,

while the maximum determinable column length is the maximum cross section that the mathematics could detect from the experimental data. Both of these plots reveal, as might be speculated, that reactivity is inversely proportional to crystallite size. A hypothesis that would account for this is that smaller crystallites could make more surface area available and gas-solid reactions are first order with surface area. Smaller crystallites could also increase gas accessibility through the interstitial volume between the crystallites.

Figs. 10 and 11 show the RMS strain at average column length and at the column length with the maximum frequency of occurrence. It is seen that the reactivity is directly proportional to both types of strains. It is obvious that they are not representing exactly the same effects because of the differences in the data points. They do not seem to be exactly linear functions but are slightly concave downward. A similar hypothesis to that proposed for small crystallite size might be extended to cover strain. Any process which increases the rate of crystallization would preclude the formation of large perfect crystallites or crystals. It is also true that more distortion would be introduced. Distortion represents strain which is the displacement of a crystal lattice point from its ideal position. Strain is related to potential energy stored in the crystal lattice. A lattice with higher strain (potential energy) should be more unstable or subject to reaction; i.e., stored potential energy could provide a source for the energy of reaction in the conversion process.

In Fig. 12, the Ca conversion vs. the peak full width at half maximum (FWHM) of the 202 XRD peak is plotted. This set of data is directly proportional to reactivity and seems to be quite accurate. This would be a reasonable result because decreasing crystallite size and increasing strain both contribute to peak broadening.

It is seen that, in the plot of conversion vs. maximum determinable column length (Fig. 9) and vs. strain at average column length (Fig. 10), the data points for the sample Fredonia are severely displaced from where they would be expected to lie. When the curve fitting had been carried out for the Fredonia 101 and 202 peaks they could not be fitted very well with the split Pearson VII function where it had provided good fits for the rest of the data. It was found that the experimental data could be fit properly if two components were used: a narrow peak and a broad peak. When the resulting data were processed and the results weighted for the respective peak areas, the Fredonia data points fell where they should. The x-ray microstructure data might imply that the sample consists of two populations: a greater component of smaller and/or more strained crystallites, and a lesser component with larger and/or less-strained crystallites.

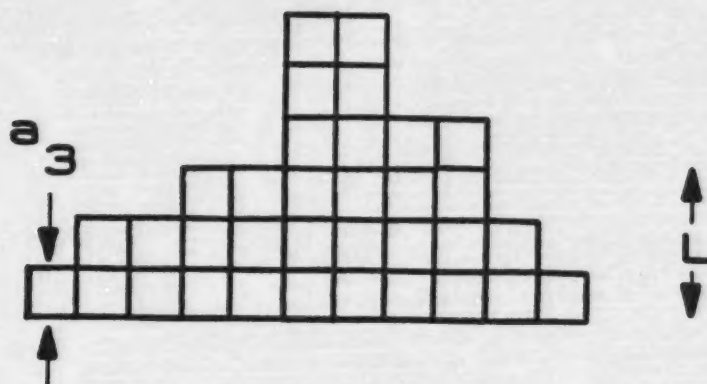
CONCLUSION

It appears that microstructure factors as obtained from x-ray diffraction peak profile analysis can provide a reliable means for predicting reactivity of Ca(OH)_2 sorbents with SO_2 .

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* Delft University of Technology, Delft, The Netherlands.



$$L = n a_3 = \text{column length}$$

Figure 1. Crystallite model showing surrogate cells and columns.

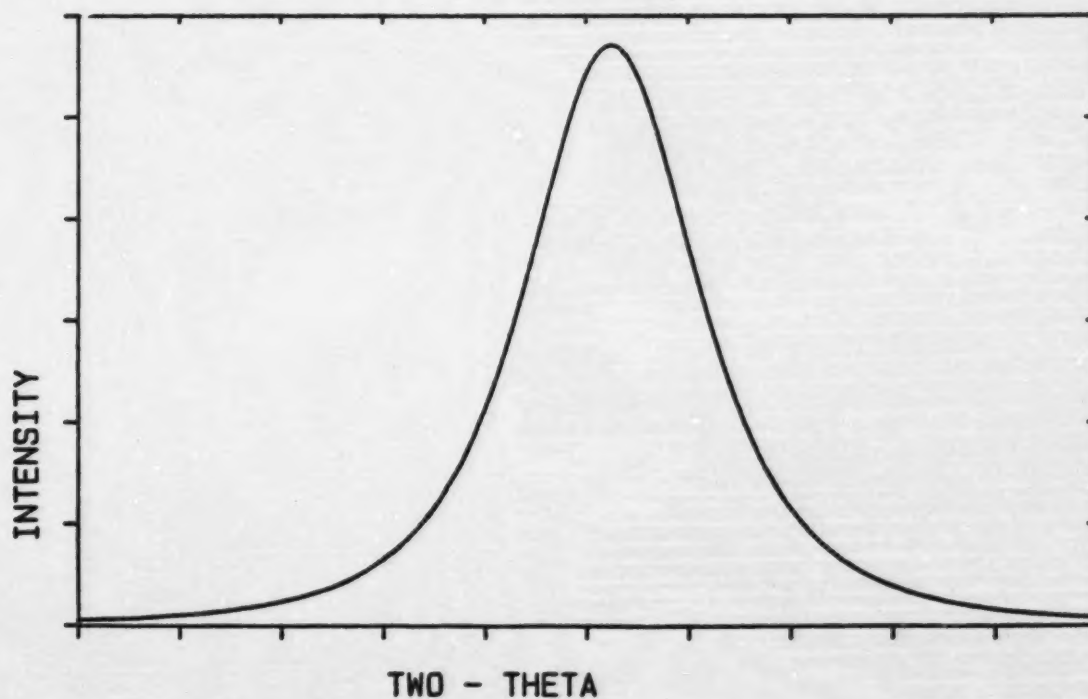


Figure 2. X-ray diffraction peak.

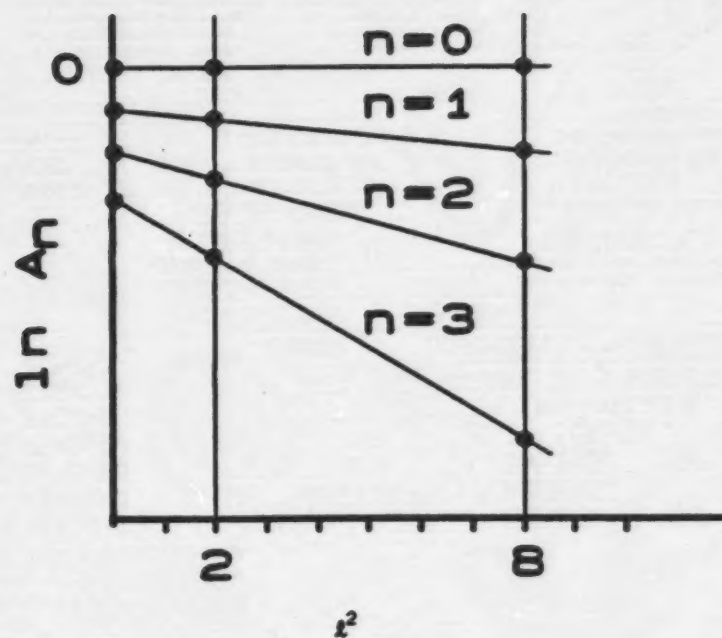


Figure 3. Plot of the logarithm of the general Fourier coefficient A_n vs. reflection order squared for $n = 0$ to 3.

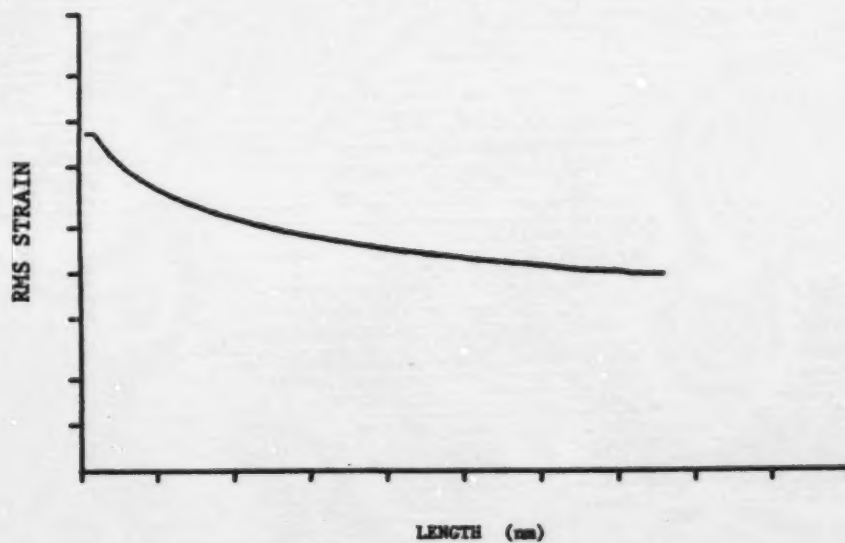


Figure 4. Plot of RMS strain as a function of column length.

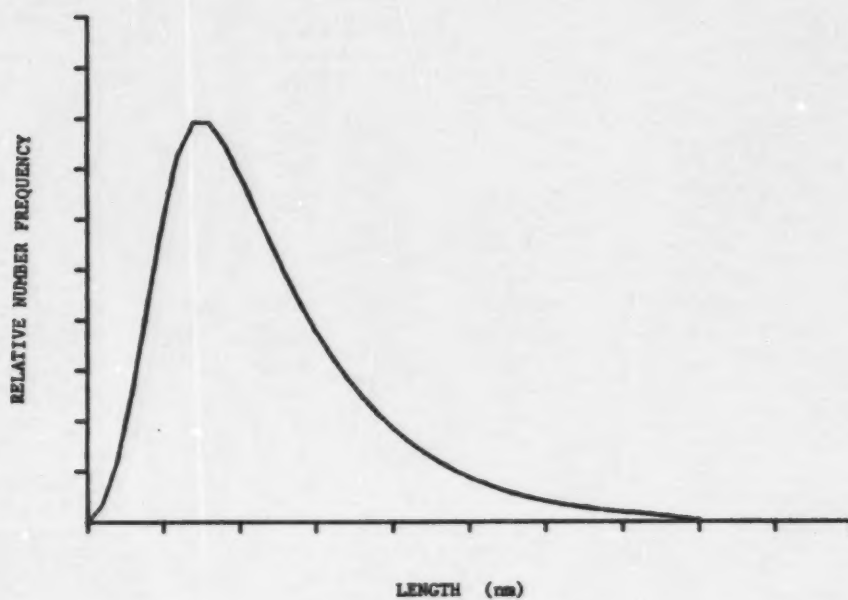


Figure 5. Plot of frequency of occurrence of column lengths vs. column length.

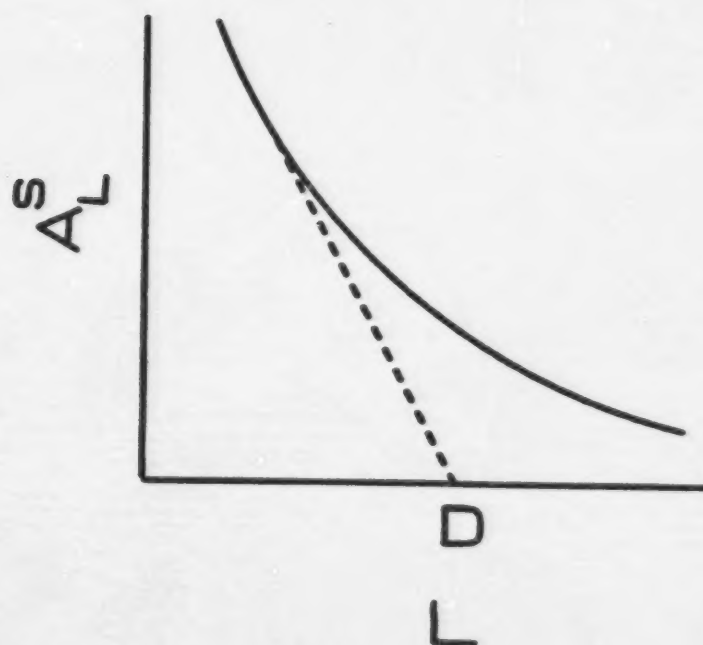


Figure 6. Plot of size coefficient vs. column length.

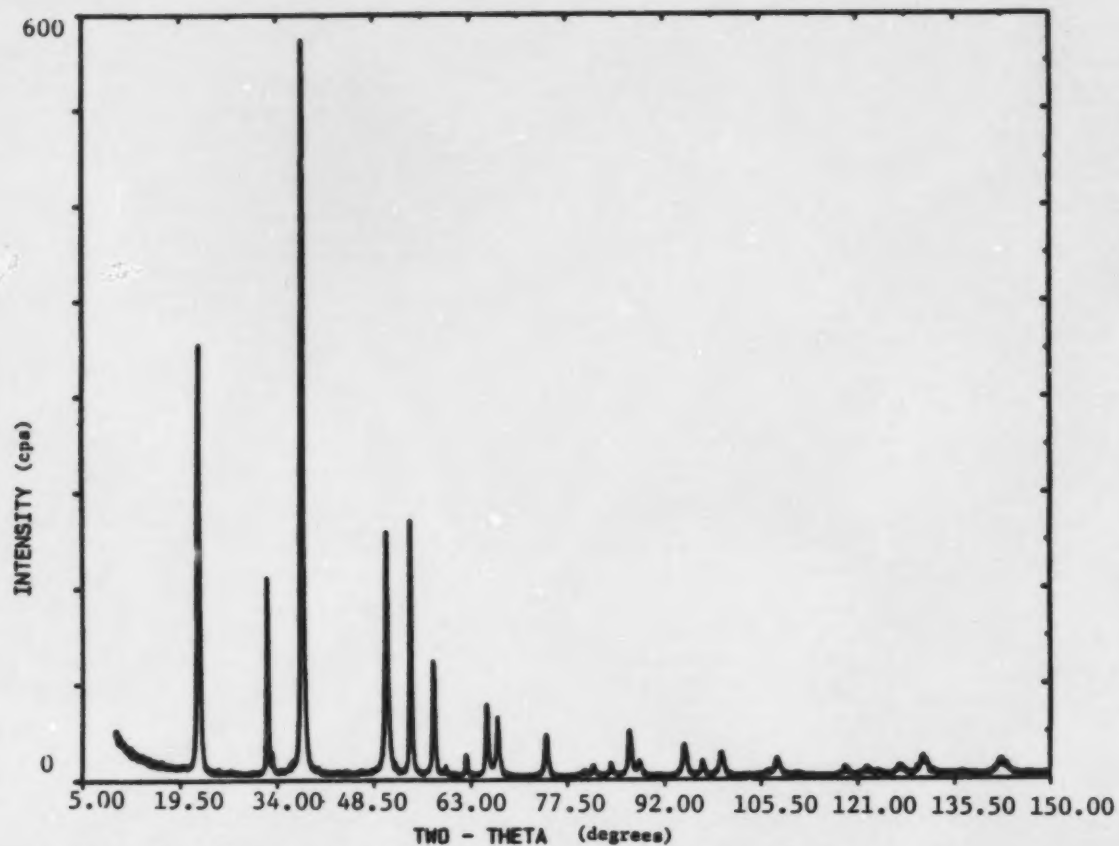


Figure 7. X-ray diffraction spectra of calcium hydroxide.

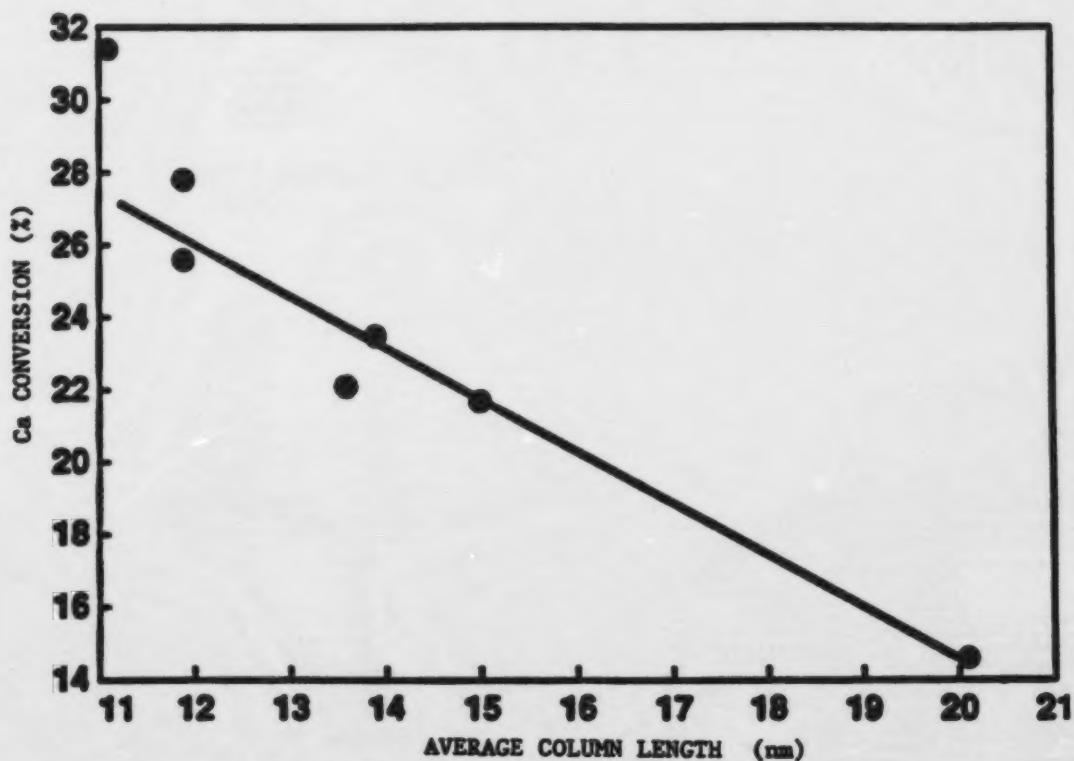


Figure 8. Plot of Ca conversion vs. average column length.

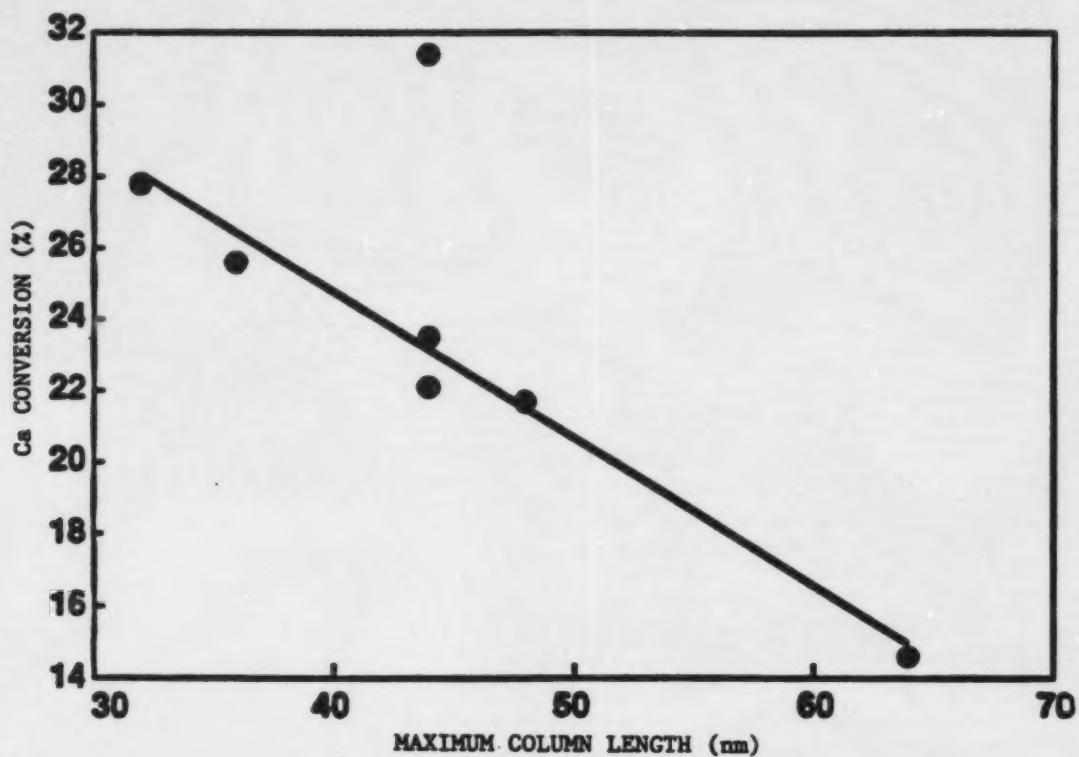


Figure 9. Plot of Ca conversion vs. maximum determinable column length.

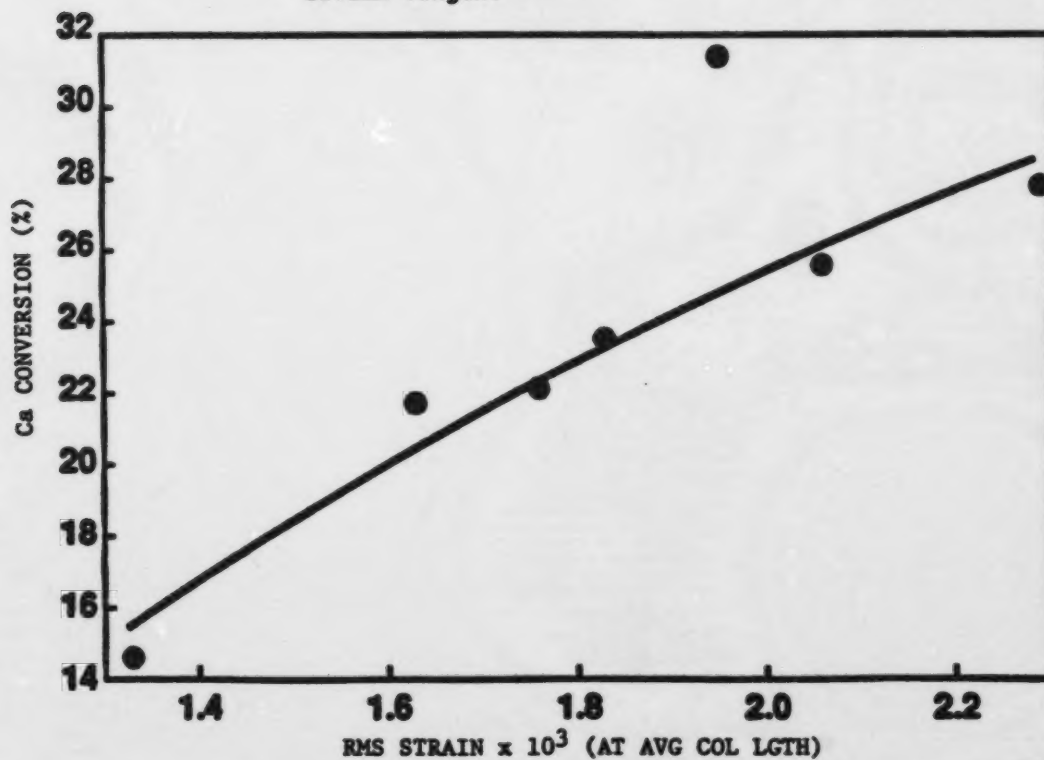


Figure 10. Plot of Ca conversion vs. RMS strain at average column length

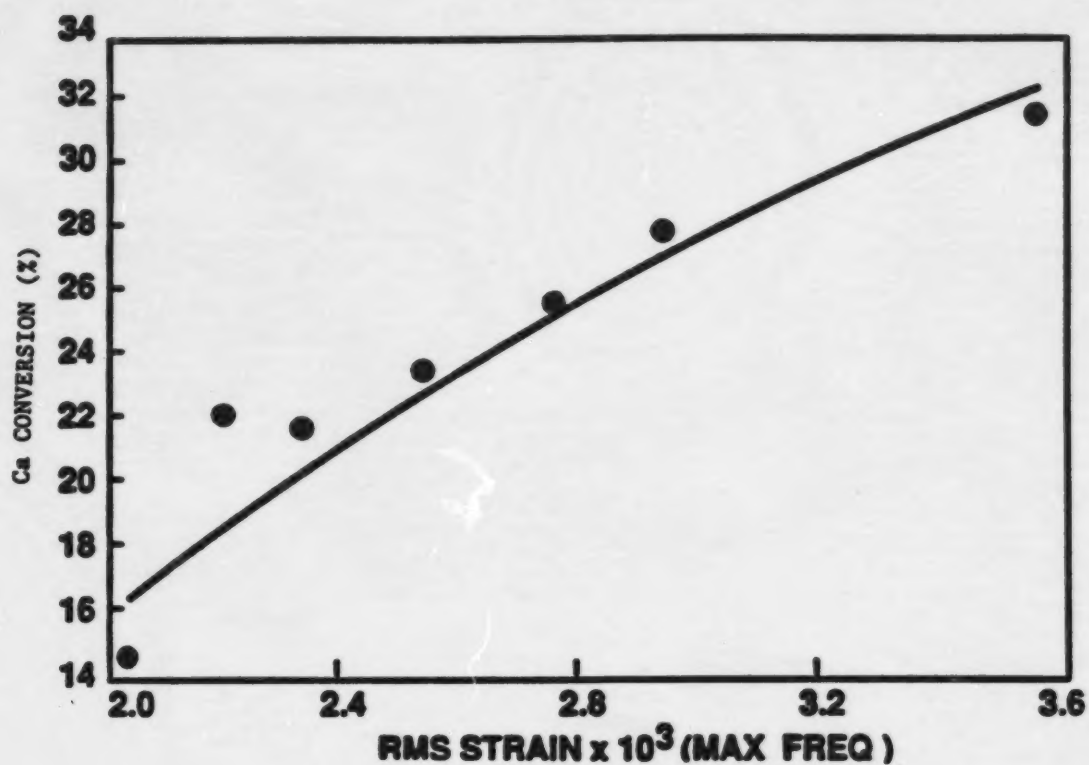


Figure 11. Plot of Ca conversion vs. RMS strain at the column length with maximum frequency of occurrence.

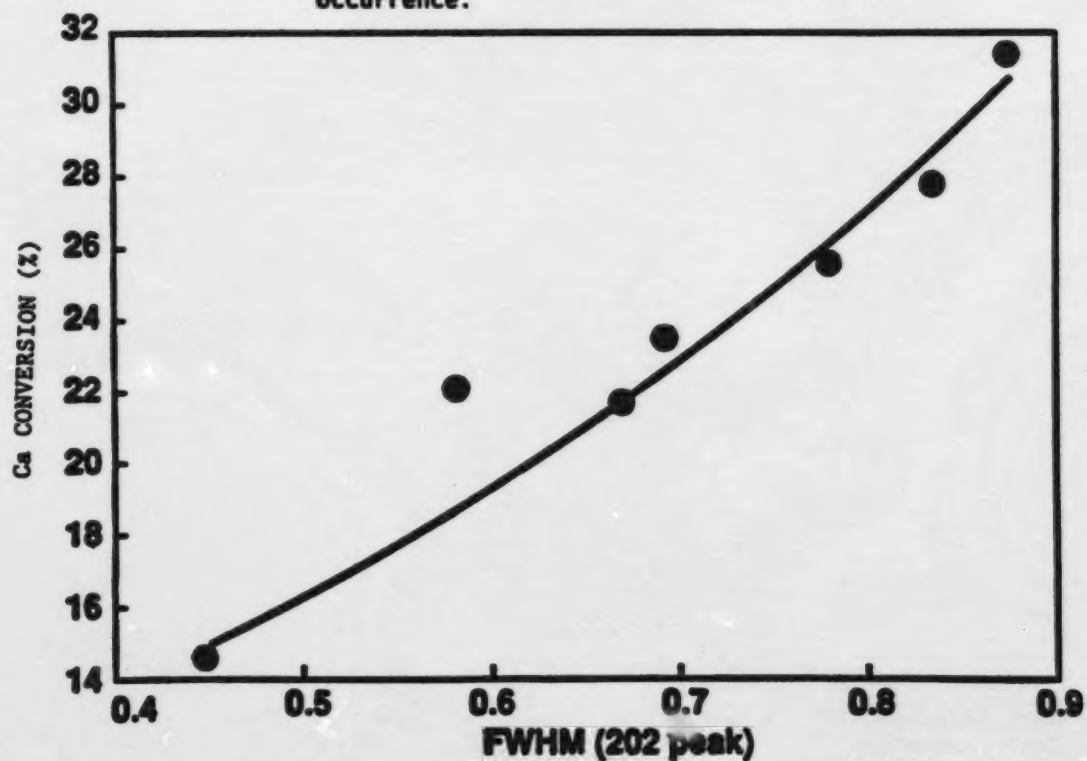


Figure 12. Plot of Ca conversion vs. x-ray diffraction peak half-width.

TABLE 1. CRYSTALLITE DIMENSIONS OF SORBENTS

Sample	Conversion, %	Average column length, nm	Maximum determinable column length, nm
Reagent	14.6	20.1	64
Koping	21.7	15.0	48
Linwood	22.1	13.6	44
0% Lig.	23.5	13.9	44
4% Lig.	25.6	11.9	36
1.5% Lig.	27.8	11.9	32
Fredonia	31.4	11.1	44

TABLE 2. LATTICE STRAINS ($\times 10^{-3}$) AND PEAK WIDTHS IN SORBENTS

Sample	Conversion, %	Strain @ average column length	Strain @ max. freq. column length	XRD 202 peak half-width, degrees
Reagent	14.6	1.33	2.03	0.45
Koping	21.7	1.63	2.32	0.67
Linwood	22.1	1.76	2.19	0.58
0% Lig.	23.5	1.83	2.54	0.69
4% Lig.	25.6	2.06	2.74	0.78
1.5% Lig.	27.8	2.29	2.94	0.83
Fredonia	31.4	1.95	3.54	0.87

SESSION 7B: NEW TECHNOLOGIES

Chairman, Charles B. Sedman, EPA/AEERL

TEST RESULTS ON THE USE OF A CIRCULATING FLUIDIZED BED ABSORBER (CFBA) FOR CONTROL OF SO₂

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Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, Ohio

ABSTRACT

A novel reactor, named the circulating fluidized bed adsorber (CFBA), has been built and is currently under evaluation as a simple method for control (either retrofit or incorporated with a new design) of SO₂ from high sulfur coal sources. The reactor involves contacting a pulverized dry sorbent such as sodium bicarbonate, limestone, lime, or calcium hydroxide with the SO₂ laden flue gases in a fluidized bed reactor operated at high velocities. A solid-gas separator, located downstream of the reactor, concentrates unused sorbent for recycle and subsequent reuse for additional SO₂ capture. The specific advantages of the system over existing dry flue gas desulfurization systems include ease of retrofitting to existing sources, isothermal operation, applicability to a variety of solid sorbents, high utilization of solid sorbents, and minimization of combustion system disruption. The results to date have shown that over 90% SO₂ removal is obtainable with sodium bicarbonate sorbents with sorbent utilizations of over 90%. Particle attrition within the reactor is seen as one reason why high sorbent utilizations are achieved.

INTRODUCTION

With the recent emphasis shown by both Federal and state energy agencies for research and development of sulfur dioxide removal systems, new and interesting methods for control of this pollutant are being proposed. These systems are anticipated for use on existing sources as retrofit control measures, and for possible new generation flue gas desulfurization (FGD) techniques for the power plant of the 1990's. For utility application, the FGD system is the second most expensive capital cost exceeded only by the boiler itself while the maintenance cost for the FGD system may range as high as 20 times the maintenance cost for the remainder of the plant (1). The amount of megawattage treated by FGD systems will undoubtedly double within the next decade and will most likely triple due to acid rain legislation (2). This represents a tremendous investment in environmental control by the United States.

A new concept, entitled the circulating fluidized bed absorber (CFBA) has been proposed and is currently under investigation at the University of Cincinnati.

This system offers promise as a low cost retrofit SO₂ control device. The project, funded by the Ohio Coal Development Office (Columbus, Ohio) is currently evaluating low temperature sorbents for reaction with SO₂ and will be evaluating calcium based sorbents in the future.

PROJECT OBJECTIVES

This two year study will address the technical questions concerning the reactor operation. Specific areas for investigation include:

- 1) Reactor Operating Parameters.
- 2) Type of Sorbent.
- 3) Effect of Sorbent Particle Size.
- 4) Energy Requirements.

SYSTEM DESCRIPTION

The experimental CFBA consists of seven major sections: (1) gas heating system, (2) flow control system, (3) fluidized bed reactor, (4) sorbent injection system, (5) particle recycle system, (6) gas sampling system, and (7) temperature and pressure monitoring system. The system is shown schematically in Figure 1.

RESULTS AND DISCUSSION

As discussed previously, various sorbents are to be evaluated in the CFBA. Testing has commenced on sodium bicarbonate and will include lime and hydrated lime in the near future. The sodium bicarbonate samples have been supplied the Church and Dwight Co., Inc., and have been designated according to their manufacturer as Type 1,2,3 or 5, according to their size distribution.

The gas flow velocity (U) required for the particles to be in the turbulent fluidized regime was determined from the following criterion (3)

$$U > 3U_{t,min}$$

where $U_{t,min}$ is the terminal velocity of the particles belonging to the smallest size for a particular distribution. A sieve analysis of three of the sodium bicarbonate samples showed the sample to possess a log-normal distribution with mass mean diameters as follows; Type 1-58 μ m, Type 2-90 μ m and Type 5-155 μ m. The terminal velocities for these three distribution were then calculated to all be less than 1 m/s according to the above relationship. Because of its larger overall size characteristics, and thus its longer retention within the reactor, Type 5 was chosen for further studies involving SO₂ removal efficiencies.

A series of experiments designed to test the isothermal assumption of the reactor along with the pressure drop along the length of the reactor due to solids injection was conducted. The results showed that with the inclusion of solids

within the reactor, the temperature drop from the reactor inlet to the outlet was approximately 40°F as compared to a 40°F loss without solids. Pressure drop, as anticipated, is a function of solids loading within the reactor and may be used as an indication of the amount of sorbent available for reaction.

The results from a series of long term (>8 hours) tests for Type 5 sodium bicarbonate are given in Figure 2. These data were obtained at a stoichiometric ratio of fresh sorbent to inlet sulfur dioxide of 1.0 (stoichiometric conditions require 2 moles of NaHCO_3 to react with 1 mole of SO_2) and an inlet SO_2 concentration of 3000 ppm. The reactor temperature range was between 254-375°F and the superficial reactor velocity was 2.3 m/s. As shown in Figure 2, the SO_2 removal efficiency varied from ~30% at low reactor solids concentration (recycle ratio @ 3) to over 90% at higher reactor solids concentration (recycle ratio @ 256). An analysis for sulfur in the waste solids verified that steady state conditions were achieved in the tests shown in Figure 2.

Also shown in Figure 2 is the overall reactor pressure drop at the various reactor solids loadings conditions. The pressure drop varied from -0.05 in- $\text{H}_2\text{O}/\text{ft}$ - 0.425 in- $\text{H}_2\text{O}/\text{ft}$ over the range of solids loadings tested.

The analysis for sulfur content in the waste sorbent revealed the sulfur uptake to be a function of sorbent particle size. The waste solids were sieved and analyzed for sulfur content (Leco Model 571), and the results compared to the theoretical maximum for sodium sulfate. The results are not surprising in light of previous results (4) but they do indicate a salient feature of the CFBA. Particles in residence within the CFBA are continually attriting to smaller particles until such time that they are either withdrawn from the ash recycle leg or escape capture by the cyclone and pass from the system. This attrition helps expose new unreacted surface area for continual reaction with SO_2 . This attrition phenomenon works to increase the overall sorbent utilization and achieve the high SO_2 removal efficiencies seen in Figure 2. Particle attrition is illustrated in Figure 3 where the size distribution of fresh, unreacted NaHCO_3 (Type 5) is compared to that of a sample of reacted sorbent. The fraction of particles from ~180-250 μm are seen to decrease due to attrition within the reactor while that fraction below 180 μm is seen to increase.

CONCLUSIONS

A circulating fluidized bed absorber (CFBA) has been built and preliminary tests have been conducted on the feasibility of using the system in conjunction with sodium bicarbonate sorbents for the control of SO_2 from flue gas. The results given in this paper show that over 90% SO_2 removal is achievable with a 90% utilization of the sorbent for a reactor temperature of 254-370°F. Pressure drop depends on solids loading to the reactor but was always below 10 in- H_2O . The sodium bicarbonate particles undergo a change in particle size distribution due to attrition, which allows for a higher sorbent utilization. The CFBA is seen as a logical contacting method for dry sorbents with sulfur dioxide laden stack gas with many attributes not seen in other FGD technologies.

ACKNOWLEDGEMENTS

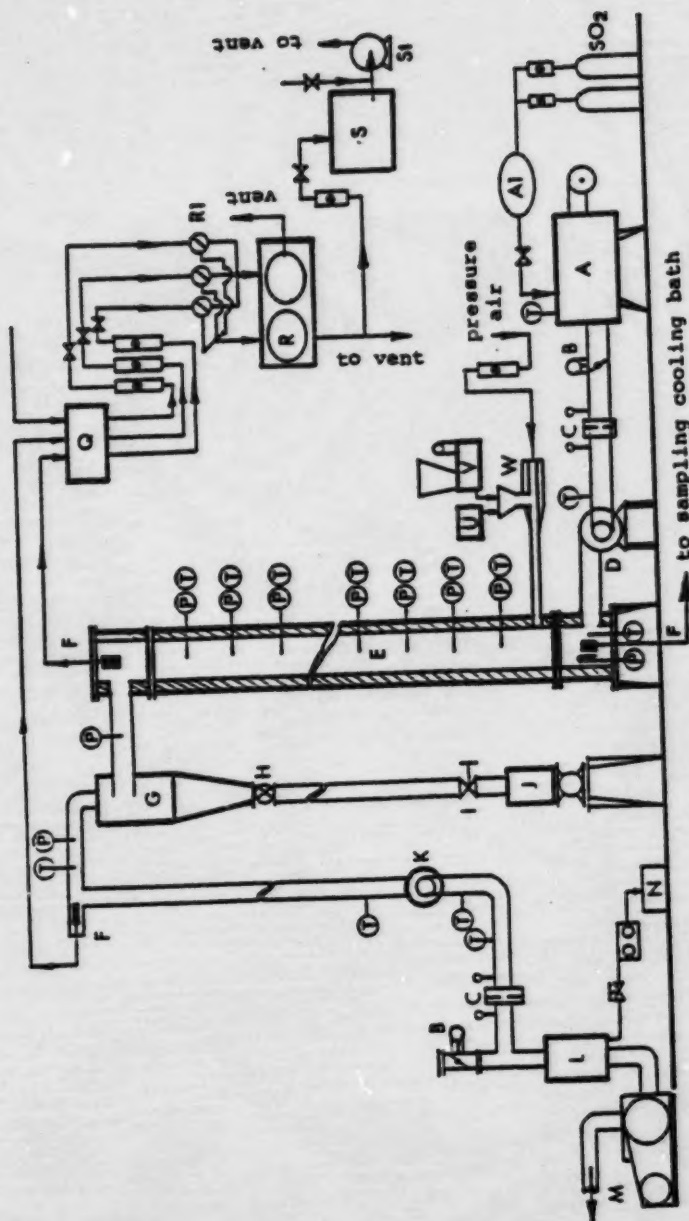
The authors would like to express their appreciation to the Church and Dwight Corporation for supplying the sodium bicarbonate materials used in this work.

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4. T.C. Keener, W.T. Davis, "Study of the Reaction of SO₂ with NaHCO₃ and Na₂CO₃," JAPCA, 34:651-654 (1984).

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.



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|-----|----------------------|----|---------------------------------|-----|--------------------------|
| A. | Gas heater | H. | Rotary feeder | Q. | Sampling cooling bath |
| AI. | Gases mixing chamber | I. | Butterfly valve | R. | Sampling pump |
| B. | Fluidized bed | J. | Recycle sorbent collecting tank | RI. | Three ways valve |
| C. | Orifice | K. | Heat exchanger | S. | SO ₂ analyzer |
| D. | Inlet fan | L. | Air filter | SI. | Sampling pump |
| E. | Sampling line | M. | Roots blower | U. | Fresh sorbent feeder |
| F. | Cyclone | N. | Condensing water container | V. | Recycle sorbent feeder |
| | | | | W. | Venturi injector |

Figure 1 Scheme of Experimental set-up

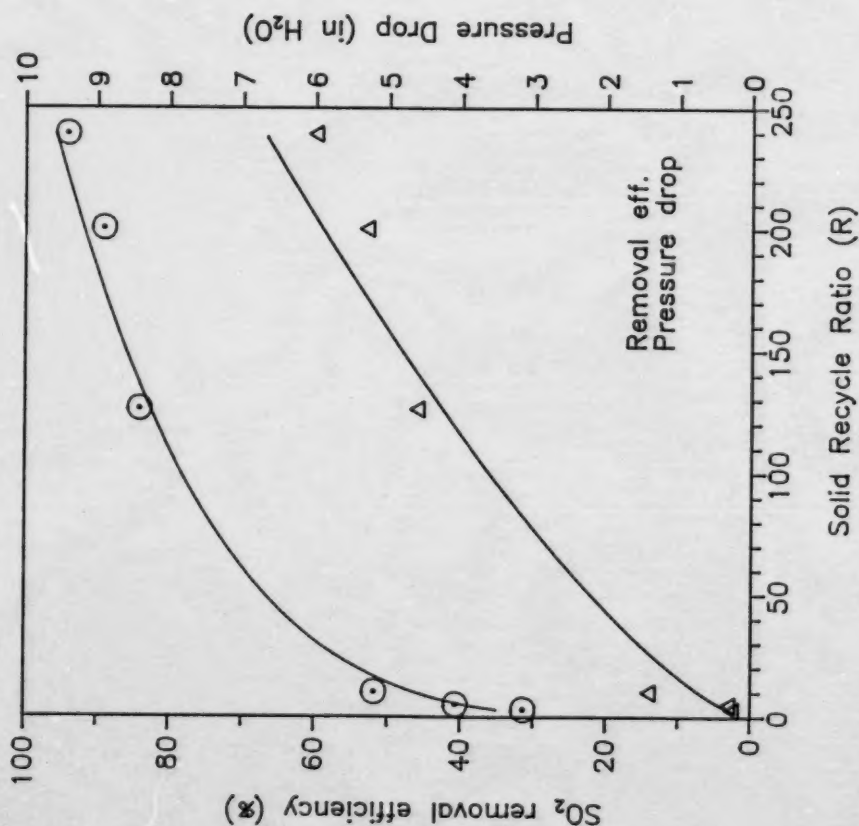


Figure 2 Test of SO₂ Removal Efficiency vs. Solid Recycle Ratio and Overall Reactor Pressure Drop (T: 254-375 °F, SO₂ conc: 3000 ppm, v: 2.3 m/s)

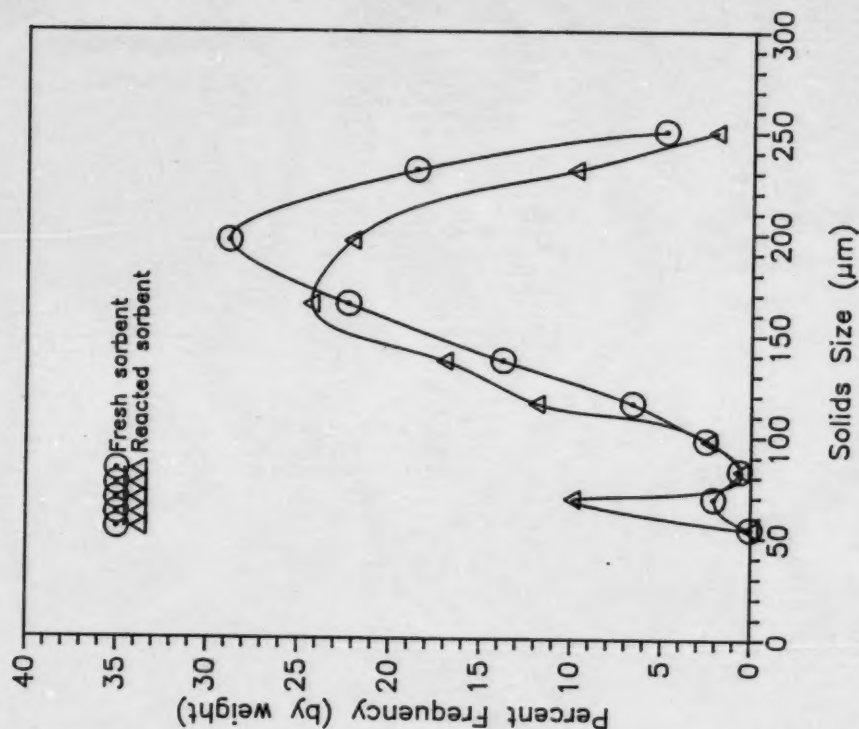


Figure 3 Comparison of Particle Size Change for NaHCO₃ type #5 (MMD: 170 μm, T: 254 °F, Recycle Ratio: 200)

A PILOT DEMONSTRATION OF THE LIMESTONE EMISSION CONTROL
(LEC) SYSTEM

by:

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James E. Wright - ETS, Inc., Roanoke, VA
Dr. Michael E. Prudich - Ohio University, Athens, Ohio

ABSTRACT

This paper describes results of a program funded by the Ohio Coal Development Office in which a Limestone Emission Control (LEC) pilot plant was installed and tested on the slipstream of Ohio University's coal-fired boiler.

The LEC is a flue gas desulfurization system employing a fixed bed of granular sized limestone to remove SO₂ from coal-fired boiler flue gases. The system is being developed to enable boiler operators to burn high sulfur coal in both an economical and environmentally acceptable manner.

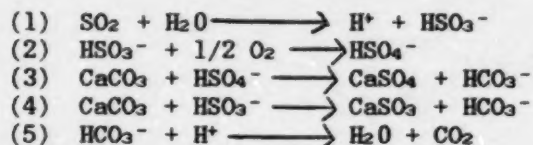
Over 100 experimental runs were made with flue gases having SO₂ contents ranging from 500 to 3500 ppm. Results show the LEC capable of 99% SO₂ removal. An average of greater than 90% removal was achieved over extended operation during which the limestone bed was regenerated several times. Favorable economic comparisons of the LEC with wet scrubbing and spray drying technologies are presented.

TECHNICAL BACKGROUND

The subject of this paper is a flue gas desulfurization process

known as the Limestone Emission Control system or LEC. In the LEC process, hot flue gases are contacted with a fixed bed of 1/32 to 1/4 inch limestone granules covered with an adsorbed layer (or a thin film) of water.

Sulfur dioxide is absorbed from the flue gas into the water and subsequently reacts with the limestone. It is generally agreed that the absorption reaction proceeds according to the following steps:



A layer of reaction products, calcium sulfate (CaSO_4) and calcium sulfite (CaSO_3), forms on the surface of the limestone granules as the reaction proceeds. Particulate matter such as flyash is also deposited in the water film.

Accumulation of reaction products and flyash on the limestone surface tends to retard the rate of reaction. When the SO_2 removal efficiency of the bed drops below an acceptable level or the pressure drop across the bed reaches the maximum allowable, the flue gas flow through the bed is stopped and the limestone granules are removed for regeneration. During regeneration, the layer of reaction products and previously captured flyash are removed from the granules exposing a fresh layer of reactive limestone. The limestone is then ready for reuse in the reactor. The reaction products can be disposed of in a landfill or considered for utilization as a raw material for the manufacture of wallboard or cement products.

In the early 1970's, the U. S. Department of Energy initiated bench-scale testing of dry limestone for flue gas desulfurization. Shale and Steward⁽¹⁾ reported that SO_2 removal efficiencies of greater than 90% for extended periods of time were possible, and that the limestone granules were regenerated easily with mild agitation. This early work resulted in U.S. patent, No. 3,976,747, titled, "Modified Dry Limestone Process or Control of Sulfur Dioxide Emissions." DOE has granted an exclusive license for this patent to ETS, Inc.

ETS, Inc. began development work on the present LEC system in mid-1982. In June, 1983, ETS and the U.S. EPA agreed that the LEC was potentially a simple, low cost FGD system. It was agreed to proceed along three paths:

1. ETS performed a series of bench scale slipstream tests to verify the basic SO_2 emission reduction. Results showed greater than 90% SO_2 removal.
2. EPA/IERL requested that TVA do a preliminary economic analysis of the LEC system. The resulting analysis was in agreement

with preliminary ETS economic studies showing that the LEC process offers significant economic advantage over both spray drying and wet scrubbing systems.

3. EPA/IERL initiated an in-house laboratory bench-scale study of the LEC process aimed at verification of the ETS slipstream tests.

Although Step 3, EPA/IERL's in-house work, was not formerly published, ETS arrived at two significant conclusions based on the EPA bench scale testing program. First, EPA's bench scale tests using simulated flue gases adequately substantiated ETS's slipstream test results and Shale's early work at DOE. And second, although regeneration of the spent limestone was demonstrated, the regeneration was not accomplished as easily as that reported by Shale and Stewart; i.e., more vigorous grinding was required.

In the fall of 1986, the Ohio Coal Development Office granted a research award to Ohio University to design, install and operate a small LEC pilot unit on a slipstream of exhaust gas from the Ohio University steam plant boilers. This research program was recently completed, as reported by Prudich and Wright⁽²⁾, and is the subject of this paper.

TEST OBJECTIVE

The LEC pilot plant tests at Ohio University had three primary objectives:

- (1) Establish optimal conditions and resulting performance for long term operation.
- (2) Establish regeneration requirements.
- (3) Interpret test results in terms of LEC system design and economics.

TEST EQUIPMENT

A schematic of the LEC pilot unit installed at Ohio University is shown in Figure 1. A slipstream of up to 400 ACFM was withdrawn from the outlet duct of the University Steam Plant ESP by an induced draft fan. The hot flue gas first entered a 40 cubic foot insulated spray chamber. A water atomizer located at the top of the spray chamber sprayed water concurrently into the flue gas to cool and humidify the gas. Steam injection ports were located in the bottom of the chamber. Steam was used to humidify the gas without cooling it. The combination of the water atomizer spray and the steam injectors provided the capability of simulating conditions obtainable by spray cooling in a large system where external heat losses would be less than that existing in the pilot plant.

After leaving the spray chamber, the humidified gas entered the LEC reactor. SO₂ concentration, temperature and humidity of the gas were measured at this point.

The LEC reactor assembly consisted of an inner basket of limestone (Figure 2) contained in an outer insulated reactor housing (Figure 3). The inner basket could be removed from the outlet housing to facilitate loading and unloading the limestone. The outer housing was equipped with a multiple-head water sprayer arrangement which allowed introduction of water directly onto the limestone bed.

After leaving the reactor, the treated flue gas was sampled for SO₂ concentration, temperature and humidity. The gas then passed through the I.D. fan and was returned to the ESP outlet duct. Flow rate control was accomplished with two manual butterfly valves, one located just below the inlet expansion chamber, and the other located on the outlet of the I.D. fan.

Continuous SO₂ analyzers were used to measure the LEC inlet and outlet SO₂ concentrations. Two types of instruments were used: a portable electrochemical type and a mass spectrometer. Both instruments were of the extractive type. SO₂ concentrations were also periodically measured using EPA reference Method 6.

Inlet and outlet gas flow rates were measured with calibrated orifices. Standard pitot tube measurements of the gas velocity were used to correlate orifice pressure drop and temperature with flow.

Gas temperatures were measured using Type J thermocouples, stainless steel dial thermometers, and mercury bulb thermometers. The LEC bed temperature profile was measured with thermocouples inserted at various depths within the limestone bed.

The moisture content of the gas streams was measured using wet/dry bulb thermometers and by EPA reference Method 4.

TEST RESULTS

A total of 106 experimental runs were conducted on the LEC pilot unit between May 28, 1987 and December 18, 1987. Three different Ohio limestones covering the full range of Ohio limestone compositions were used in these tests. The program studied the effects of varying limestone bed depth (from 6 to 18 inches), superficial flue gas velocity (from 1.0 to 2.0 feet per second), flue gas humidity, flue gas SO₂ concentration, and flue gas temperature. Several methods of adding moisture to the LEC bed were also studied, including water atomization into the flue gas, direct over-bed water spray, and steam injection into the flue gas.

Figure 4 presents the measured SO₂ removal performance under the noted (optimum) test conditions. It is considered significant that the SO₂ removal performance of the regenerated stone was found to be

essentially identical to fresh stone. An average SO₂ removal of 91.8% was recorded for 24 hour intervals between regenerations. Continuous removal above 90% was maintained for 16 hours.

TEST CONCLUSIONS

Conclusions from the LEC slipstream pilot plant testing at Ohio University were:

- (1) Pre-pilot LEC experiments had indicated the LEC process to be capable of removing greater than 90% of the SO₂ from coal-fired combustor flue gas streams. In this test series, high average removal efficiency was again demonstrated to be achievable and more importantly, was demonstrated to be sustainable for periods up to 24 hours and over a wide range of inlet SO₂ concentrations.
- (2) Two long cycle time regimes of LEC operation were identified, one involving humidified, saturated flue gas and the other involving the use of over bed water sprays. It is possible that a combination of the two approaches will prove to have the most practical applicability.
- (3) The regeneration of exhausted LEC limestone was demonstrated. Even though initial regeneration tests were made, additional work is necessary before the regeneration process can be considered optimized.

LEC SYSTEM DESIGN MODIFICATIONS

Pilot plant testing at Ohio University has shown the desirability of making two changes in the originally conceived mechanization of the LEC.

The original LEC configuration assumed that the solid reaction products formed on the surface of the limestone granules would be sufficiently friable such that vibration of the spent bed would remove the products from the limestone surface. Testing to date has shown that the reaction products can be removed for successful regeneration; however, the necessary intensity of required grinding has led to question the practicality of doing the grinding in-situ. Hence, the first configuration change being considered is the removal of the spent limestone from the bed, grinding it, then replacing the regenerated limestone back into the bed.

The original LEC configuration also assumed that adequate condensation of water from the flue gases would occur on the cold limestone surfaces to provide the moisture necessary for good SO₂ removal performance. Cold limestone was to be provided by alternately using the limestone bed as an air pre-heater. Testing has demonstrated that best SO₂ removal can be achieved by humidifying the flue gases prior to their entering the limestone bed. As a result, the second

change to the original configuration is to eliminate the air pre-heater function. Note that this change significantly simplifies the overall system, effectively eliminating 1/2 of the beds, thus offsetting the added complexity of external grinding of spent limestone.

To evaluate the economic potential of the LEC concept incorporating external grinding and not incorporating the original air pre-heater function, a preliminary design study was conducted based on a size and configuration deemed suitable for a 100 MW utility boiler burning 3.5% sulfur, 12,000 Btu/lb coal and producing 400,000 ACFM of flue gases at 300°F.

Figure 5 is a schematic of the LEC system with external regeneration. This system incorporates regeneration by dry grinding in an attritor mill, similar to the process used in the Ohio University testing.

Limestone would be removed from one bed at a time and conveyed to the regeneration grinder. Grinding may be either dry or wet. If dry grinding is used, a slipstream of hot, dry flue gases, from upstream of the spray cooler, will be directed up through the grinder to both dry the stone and to entrain the fine material dislodged from the limestone surface. After separating the fine material from the stream, these gases will be returned to the LEC inlet. Thus, the energy for drying would be derived from the main flue gases and the humidity removed would be returned to the desulfurization process.

The regenerated stone exiting the grinder is conveyed to a bed filling hopper sized to measure and hold one bed volume. Make-up stone would be added to the fill hopper as required to maintain a constant bed height.

The following key LEC reactor bed parameters, each of which was successfully demonstrated during the Ohio University testing series, were selected as a basis for the design study:

- (1) a bed superficial velocity of 1.5 ft/sec,
- (2) a bed thickness of 6 inches,
- (3) and an operational time of 8 hours between regenerations of the bed.

Using these key values, Table I lists the calculated bed dimensions for the 100 MW size. Each of the LEC beds was selected to be 12 feet by 12 feet to meet factory fabrication and shipping criteria. The necessary single bed height, including inlet and outlet plenums, is 2 feet; thus the 33 bed assembly could be stacked vertically resulting in a total height of 66 feet. Figure 6 shows such a 33 bed stack with required ducting and valving. Other multiple bed arrangements would of course be possible; available space for installation would influence the selection for a specific installation.

Figure 7 sketches a cross-section of the selected bed configuration. Note that each bed utilizes a single 3-position diverter valve for emptying and filling the bed with stone. Each of the 33 diverter valves is connected to a single vertical stone fill/dump pipe on the side of the bed stack. During normal bed operation the diverter valve is in position A, closing the passage between the bed and the vertical passage while permitting through-flow in the vertical passage. To dump the spent limestone from the bed, the diverter valve is moved to position B and the limestone bed vibrators activated causing the limestone to spill down the vertical passage. Limestone would be moved from the horizontal bed into the vertical passage by vibration of the bed base with pneumatic vibrators similar to the action of a vibrating conveyor.

To refill the empty limestone bed, the diverter valve would be moved to position C, directing limestone flowing down the vertical passage into the bed. The vibrators would be again activated, this time to level the limestone entering the bed. Regenerated limestone is supplied to the fill/dump pipe from a hopper located at the top. Regenerated limestone is mechanically conveyed from the regeneration grinder to this hopper.

Either of two fill/dump sequences appears possible. A first sequence would incorporate the filling of one bed while the bed below it is being dumped. Next, the bed just dumped would be filled while the next lower bed is dumped. This fill/dump sequence involves having two beds off-line simultaneously and would progress from top to bottom of the bed stack. An alternative fill/dump sequence involves having only one bed off-line at a time and would dump one bed then fill it before progressing on to the next bed.

This sequence would require dumping and filling rates twice the rate for the two-bed off-line sequence, but would require one less bed in the total stack. Additional testing will be required for final selection of the optimum fill/dump sequence; however, the two-bed off-line sequence was selected for the economic study.

ECONOMIC ANALYSIS OF LEC SYSTEM WITH EXTERNAL GRINDING

An economic analysis was made of the LEC design features and size (400,000 ACFM) discussed in previous paragraphs. The analysis included before-tax capital and operating costs, a discount rate of 6.1%, constant 1987 dollars, and levelization of capital over a 15 year study period.

Based on limited experience with granular bed filters in coal-fired boiler applications, the LEC system should provide satisfactory particulate removal in addition to SO₂ control for many installations. However, since this attribute of the LEC system has not been thoroughly studied, separate analyses were conducted for LEC systems with and without an electrostatic precipitator (ESP) serving as the particulate control system.

Separate equipment cost elements for the basic LEC system (no ESP) are listed in Table II. The manufacturers' selling price for the granular bed module was developed by estimating the weight for a typically sized LEC module, as shown in Table III, and applying \$1.25 per pound for fabricated metal equipment. Costs of other auxiliary equipment, including the grinding equipment, were obtained from actual manufacturer's quotes, as indicated in Table II.

Table IV compares the estimated annualized costs for the LEC system with those of both a lime spray dryer and a limestone wet scrubber. The analysis shows that the annualized cost of the basic LEC system is \$856,000, or \$47 per ton of sulfur dioxide removed. If a separate particulate removal system is required, then the addition of an ESP to the LEC system raises the annual cost to \$2,845,000 or \$155 per ton of SO₂ removed. Even with the added ESP, the LEC compares very favorable with the estimated SO₂ removal cost of \$268/ton for a spray dryer system equipped with a pulse-jet bag-house, or with the estimated removal of \$349/ton for a limestone scrubber system.

This updating of the LEC economic potential to incorporate the test parameters proven during pilot testing indicates that the system still offers significant advantages over current technology.

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- (2) Prudich, M. and J. E. Wright. "Small Pilot Plant Demonstration of ETS' Limestone Emission Control Systems." Ohio University, Department of Chemical Engineering; May 1988.

DISCLAIMER

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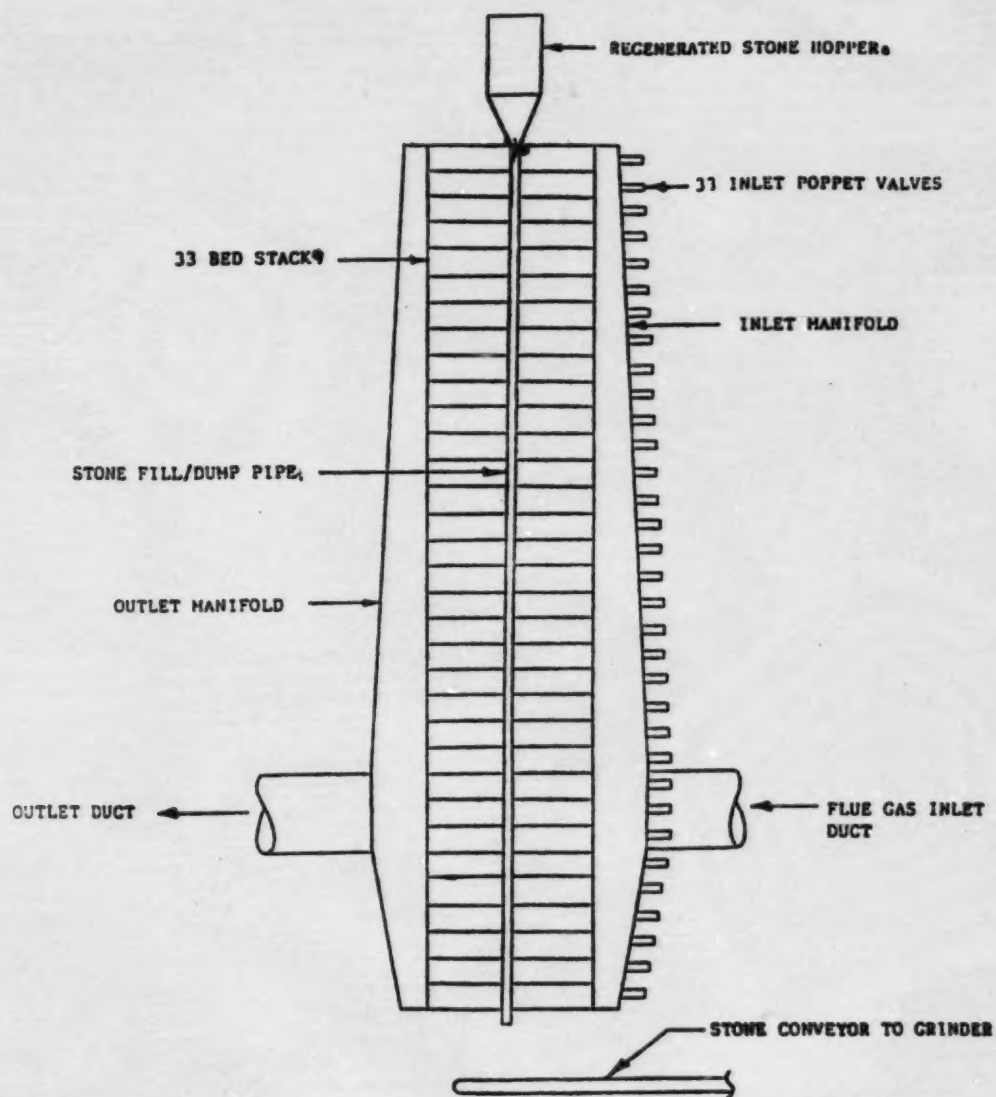


FIGURE 6 - 33 BED LEC USING EXTERNAL GRINDING

TABLE I
LEC SIZING PARAMETERS

BASIC LEC VALUES

Superficial Bed Velocity	=	1.5 ft/sec
Bed Height	=	6.0 inches
Bed On-Line Time	=	8.0 hours

BOILER PARAMETERS

Size	-	100 MW, 7000 hr/year
Gas Flow	-	400,000 ACFM @ 300°F
Coal	-	12,000 Btu/lb, 3.5% sulfur 292,000 tons/year

LEC SIZING

Total required bed area	-	4,444 ft ²
Total stone volume	-	2,222 ft ³
Individual bed area	=	144 ft ²
Number of on-line beds	=	31
Number of beds being regenerated	=	2
Total number of beds	=	33
Time available for regeneration	=	15 min.

TABLE II
INSTALLED EQUIPMENT COST ESTIMATES FOR A 400,000 ACFM LEC
UNIT WITH EXTERNAL REGENERATION

MANUFACTURERS EQUIPMENT COST
=====

Fabricated Metal (@ \$1.25/lb)	\$ 209,343
Insulation ¹ (@ \$26.27/ft ²)	124,835
Bed Dump Valves ² (66 @ \$2,600)	171,600
Inlet Poppet Valves (33 @ \$2,500)	82,500
Bed Vibrators ³ (66 @ \$709.24)	46,810
Stone Feed Conveyors (200 ft. @ \$150/ft)	30,000
Weigh Hopper and Controls	25,000
Vibrating Screen Dust Separator	18,000
Attritor Grinding Mills ⁴ (3 @ \$67,712)	203,136
	\$ 911,224
Installation (31% of Total Equipment) ⁵	282,479
Total Installed Cost (Direct Cost)	\$ <u><u>1,193,703</u></u>

¹ Derived from 1978 EPRI Study, (\$17.75/ft³ X 1.48 escal.)

² Air Industries and Resources Quote

³ Cleveland Vibrator Quote (\$606 on 6/18/84 X 1.17)

⁴ Union Process, Inc. Quote

⁵ Based on similar costs for typical spray dryer systems

TABLE III

WEIGHT ESTIMATE FOR A TYPICAL LEC GRANULAR BED

MODULE SIZE

Length	12 ft.
Width	12 ft.
Height	2 ft.

BED SIZE

Length	12 ft.
Width	12 ft.
Area	144 ft ²

MODULE DUCT

Width	12 ft.
Length	24 inches

METAL THICKNESS

3/16 inches

WEIGHTS

4	vertical walls	726 lbs.
2	duct outlet walls	363
4	duct side walls	363
1	distributor plate	2,174
1	roof	<u>1,449</u>
	Total	5,075 lbs.

TABLE IV
COST COMPARISON OF LEC SYSTEM WITH COMPLETING FGD TECHNOLOGIES

	LEC ⁽¹⁾	LEC ⁽²⁾ +ESP	SPRAYER ⁽³⁾ DRYER	LIMESTONE ⁽⁴⁾ SCRUBBER
(1) Total Turnkey Cost - \$1000 (Includes Equipment, Installation, Indirect Cost, and Contingencies)	1995	4738	8010	23995
(2) Annual Reactant Costs - \$1000/yr	271	271	1341	248
(3) Annual O&M Costs (exclud- ing Reactant) - \$1000/yr	297	1841	2352	2649
(4) Total Annual Operating Costs - \$1000/yr	568	2112	3693	2897
(5) Total Annualized Capital Charges - \$1000/yr	288	733	1243	3518
(6) Total Annualized Cost - \$1000/yr	856	2845	4936	6415
(7) Annualized Cost/Ton SO ₂ Removed - \$/Ton	47	155	268	349

NOTES:

- (1) Basic LEC system with no additional provisions for particulate removal.
- (2) Basic LEC system plus electrostatic precipitator for total particulate removal.
- (3) Spray Dryer with pulse jet baghouse.
- (4) Limestone Scrubber with forced oxidation and without particulate removal.

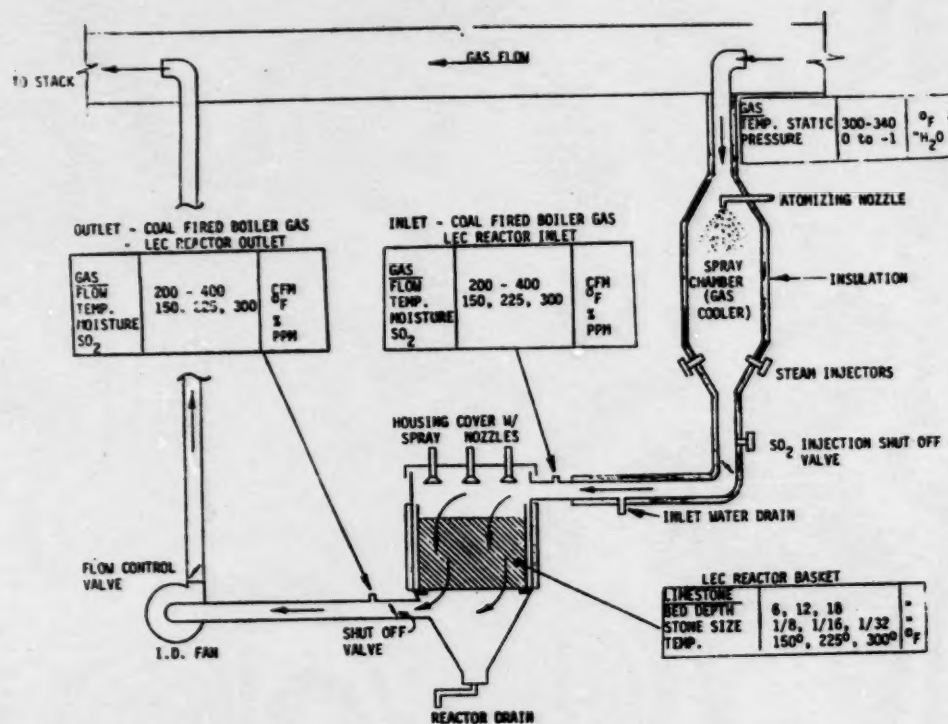


FIGURE 1 - LEC PILOT PLANT SCHEMATIC

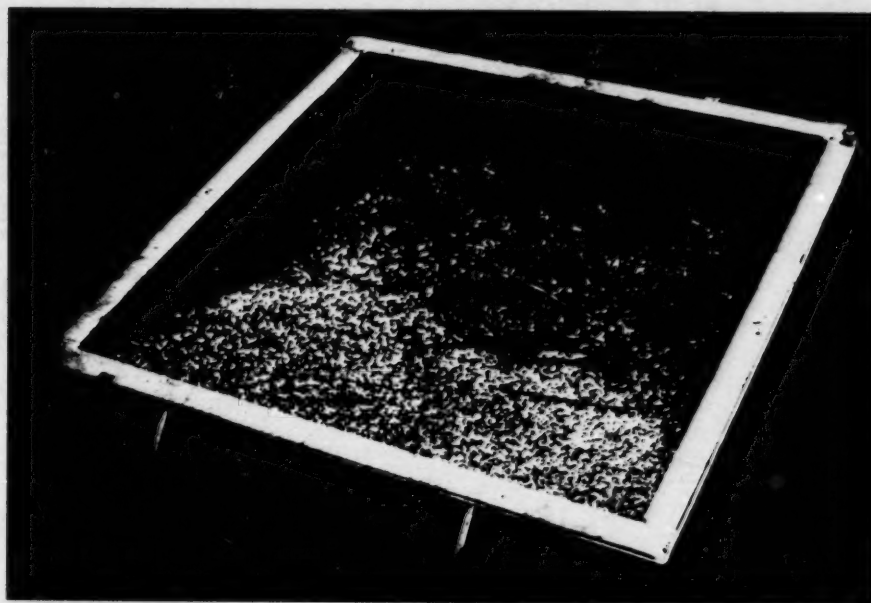


FIGURE 2 - LIMESTONE BASKET

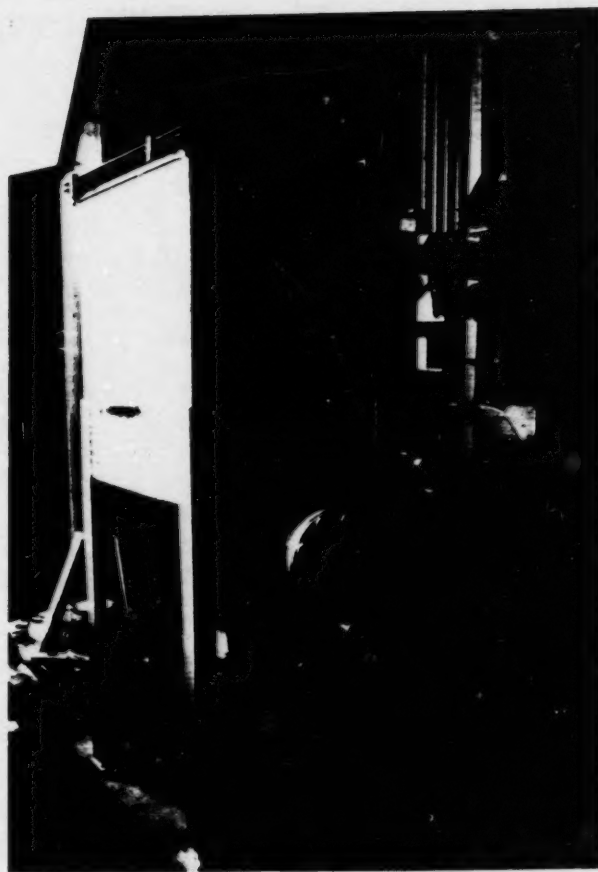
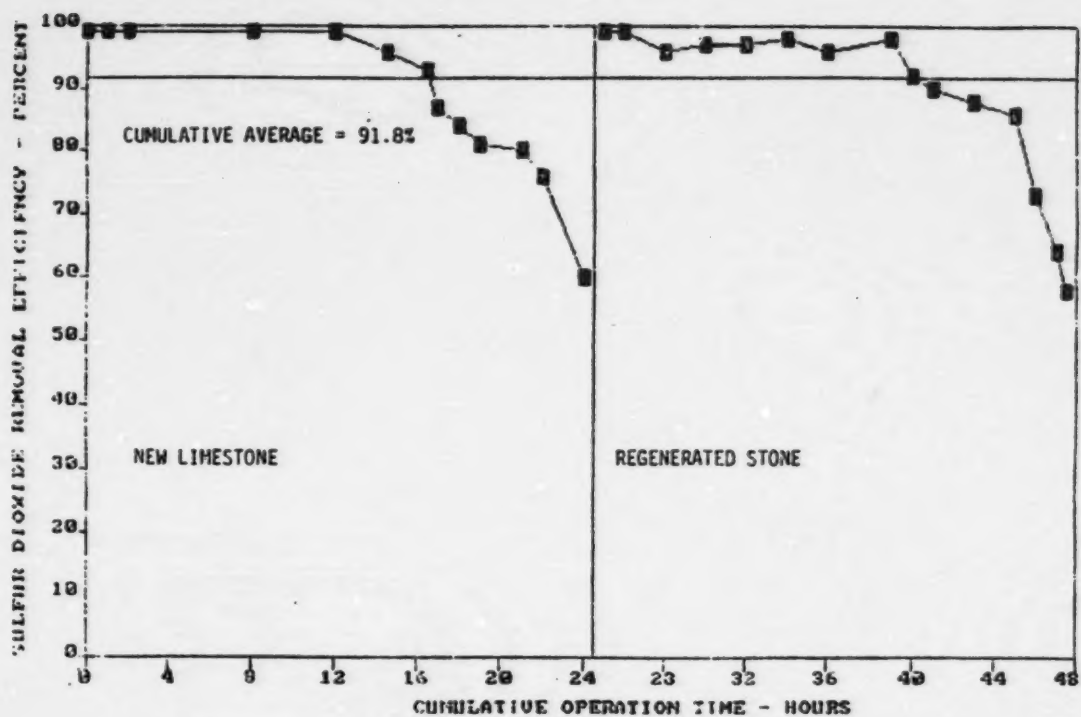


FIGURE 3 - REACTOR HOUSING



TEST CONDITIONS: Maxville Quarry Limestone; 6" Bed Depth; 1.0 ft/sec superficial gas velocity; 100% Inlet Gas Humidity.
 170-185°F Inlet Gas Temperature
 375-975 ppm (625 ppm average) Inlet SO₂ Concentration

FIGURE 4 - MEASURED LEC SO₂ REMOVAL AT OHIO UNIVERSITY WITH REGENERATION

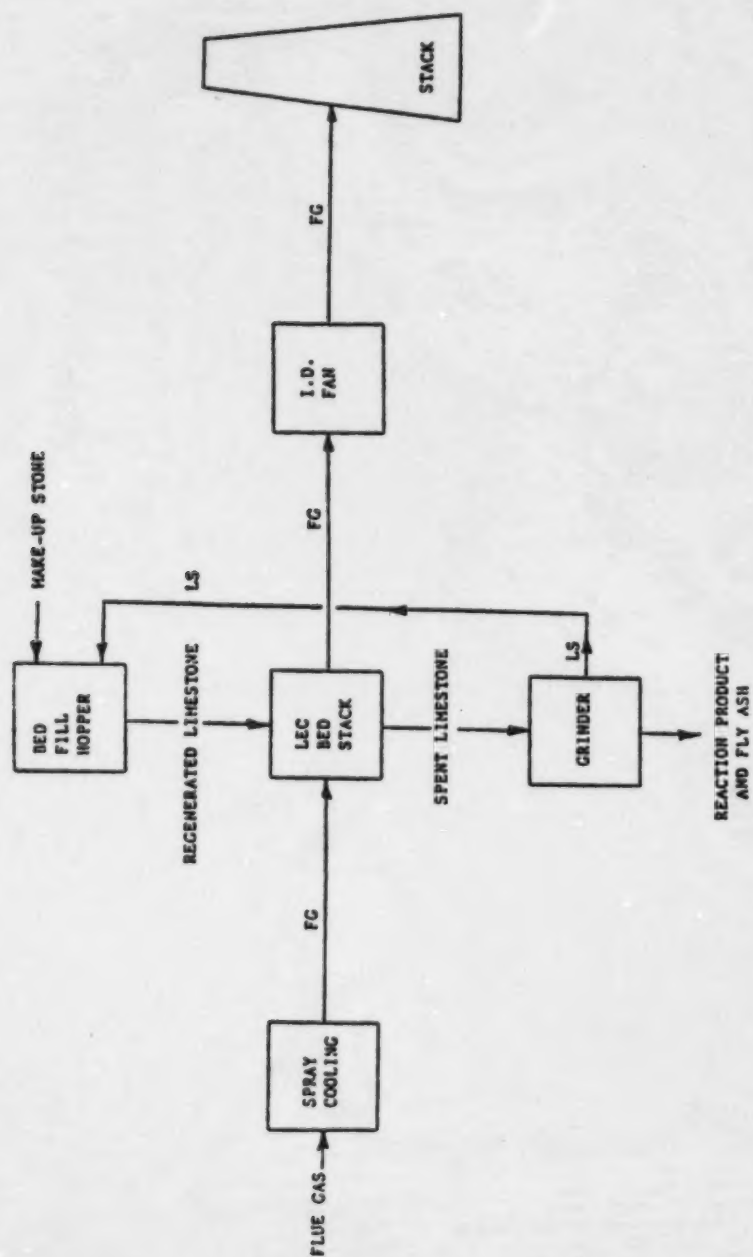


FIGURE 5 - LEC SYSTEM WITH EXTERNAL REGENERATION

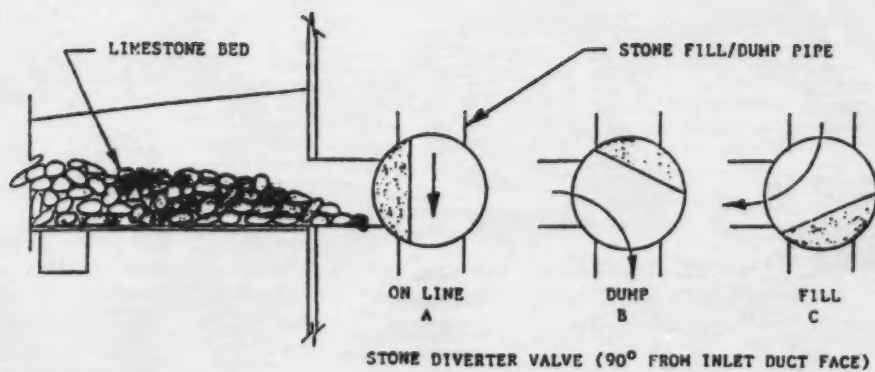
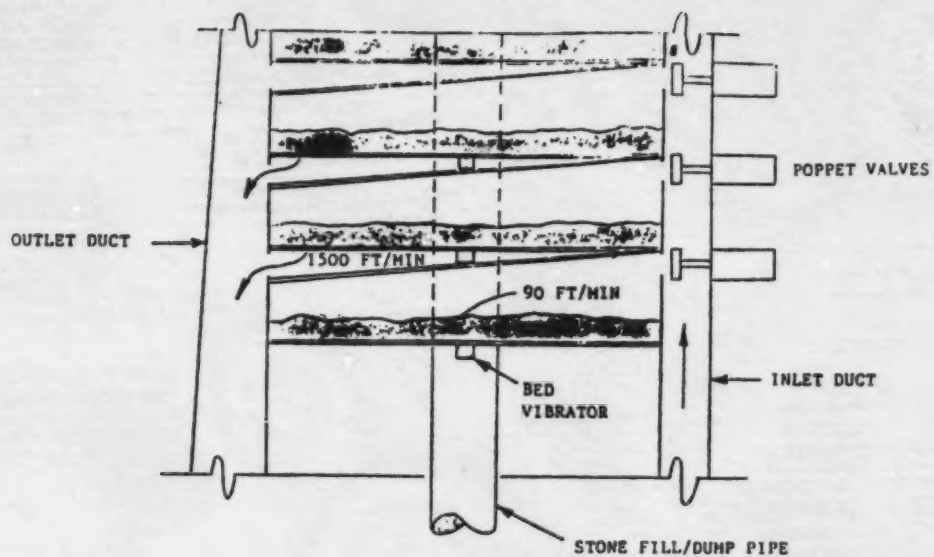


FIGURE 7 - STACKED LEC BEDS

SO₂ RECOVERY BY SODIUM PHOSPHATE SOLUTION SCRUBBING

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Prepared for EPA/EPRI
First Combined FGD and Dry SO₂
Control Symposium
St. Louis, Missouri
October 1988.

ABSTRACT

Sulfur recovery from flue gases is expected to become more attractive. A new SO₂ absorption process which supplements the earlier developed citrate and adipate absorption/steam stripping processes, is described. In this the absorbent is a concentrated sodium phosphate buffer and the loaded buffer is regenerated by evaporation. The main buffer component is Na₂HPO₄, but NaH₂PO₄ is added in order to obtain a more complete SO₂ removal during regeneration. The process promise excellent absorption properties for SO₂ with extremely low oxidation losses, regeneration with little or no incrustation problems and important energy savings.

INTRODUCTION

Flue gas desulfurization (FGD) is much in focus in industrialized countries with calcium-based processes producing gypsum in the lead. However, in several countries the amount of gypsum thus made available, is expected to outpass by far the demand. At the same time a new situation is observed which may have a strong impact on the future choice of FGD-processes: a critical supply-demand balance for sulfur is developing with a trend pointing towards a global sulfur shortage (1), (2). In 1984 the world's sulfur consumption exceeded the production by 5-6 million tons. The gap was filled from stocks, which are rapidly being exhausted.

Seen in this context the very large quantities of SO₂ present in flue gases may prove to be a very important future source of sulfur. Such gases vary strongly in SO₂ concentration, temperature, humidity, oxygen content, etc. Also emission regulations may differ locally and from country to country. Indications are therefore that there will be a growing market for FGD processes recovering sulfur, and that there will be need for a choice of such processes for meeting the different demands.

SO₂ RECOVERY PROCESS DEVELOPMENT WORK

THE CITRATE ABSORPTION - STEAM STRIPPING PROCESS

This process, best known as the Flakt-Boliden process (3), showed an "impressive technical performance" in a pilot study undertaken by the Electric Power Research Institute, EPRI (4). Absorption and regeneration take place in packed towers with small pressure losses, no solids formation and very small oxidation losses. The most serious limitation of this process concerns its application on gases with very low SO₂ contents such as are often found in thermal power plants, since the specific steam consumption, S_v, will then be too high. Another objection which was valid when the EPRI study was undertaken, concerns an elaborate method proposed for selective removal of Na₂SO₄, which accumulates in the process liquor (5). A much simpler method has since been developed, and the citrate process is now considered to be very competitive for SO₂ recovery from relatively rich gases, such as Claus tail gases and non-ferric smelter gases, (6).

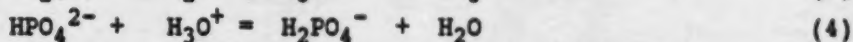
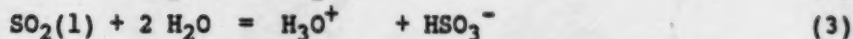
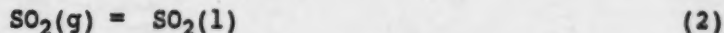
THE ADIPATE ABSORPTION-STEAM STRIPPING PROCESS

This process offers the same advantages as the citrate process, and in addition a system specific possibility for reducing S_v (6). The adipate process is suited for lower feed gas SO₂-partial pressures and for higher absorption temperatures than the citrate process. However, both of these processes will require relatively high S_v values for gases very lean in SO₂. This gave us an incentive to search for possible alternative process routes.

THE NEW PHOSPHATE ABSORPTION-EVAPORATION PROCESSES

BASIC CHEMISTRY

In the phosphate process the second dissociation step of phosphoric acid is the active buffer. The main reactions made use of are



These are instantaneous and reversible reactions. The preferred buffer is, however, a mixture of Na₂HPO₄ and NaH₂PO₄. We have discovered that nearly complete removal of SO₂ from concentrated Na₂HPO₄-buffers by boiling is possible only when the SO₂ free buffer contains a substantial proportion of NaH₂PO₄. The SO₂ absorption is carried out inside a pH-range of 4.5 to 6.5, whereas the citrate and adipate processes are operated within the pH-range 3.0-4.5. With the much higher pH, higher SO₂ loadings and also more complete SO₂ absorption can be accomplished.

EXPERIMENTAL PROCEDURES

Gas-liquid equilibrium determinations

Figure 1 shows the gas-circulation method used for the upper range of SO_2 partial pressures: A known volume of inert gas (N_2) was equilibrated with samples of SO_2 -loaded buffer. Thereafter the SO_2 content of this gas volume was absorbed in H_2O_2 -solution and determined by standard NaOH titration.

For extremely low SO_2 partial pressures (below about $4 \cdot 10^{-4}$ bar), an UV SO_2 -analyzer (Type Radas, Hartman & Braun) was used, as shown in figure 2. The instrument was calibrated with standardized gases with 40 and 385 ppmv SO_2 in N_2 , respectively. The SO_2 equilibrium partial pressure was computed from the formula

$$p_{\text{SO}_2}^* = 10^{-6} \cdot \text{ppmv} \cdot (P - \Delta p)$$

where ppmv = instrument reading, P = total pressure in the gas leaving the last gas washing bottle (the pressure drop downstream from this point to the manometer was negligible) and Δp = difference in water vapor partial pressure between the gas leaving the buffer solution and the condenser, corrected for the reduction in the water vapor pressure, caused by the salts (7).

The SO_2 concentrations of the respective buffers, were determined by iodometric titration.

Regeneration experiments

Figure 3 shows the equipment used. The evaporator was a 4 l thermally insulated glass vessel provided with a flanged lid, a stirrer placed in the center of a short cylinder which had a coil of "thermo-coax" heating cable wrapped around the outside, 4 baffles, a submerged thermocouple, etc. The vapor was led to a condenser and then into H_2O_2 solution in a gas washing bottle. Two bottles in parallel allowed continuous sampling. The amount of $\text{H}_2\text{O} + \text{SO}_2$ in each sample was determined by weighing, and the SO_2 by NaOH-titration. Each experiment was started with batchwise evaporation of a 2-3 l charge of the SO_2 -loaded buffer until a predetermined percentage of the water content had been evaporated. Then semicontinuous operation was started by means of a metering pump. The buffer supply vessel rested on a scale with digital display. This procedure allowed the water balance to be controlled throughout the experiment. An extra 2 - 3 l of SO_2 -loaded buffer was usually supplied by the pump, with a feed rate in the range 6,5 - 9,0 g/min. In all these experiments the material balances (total-, H_2O - and SO_2 -balances) came out with very high accuracy (maximum 1 - 2% deviation).

Oxidation studies

The equipment in figure 1 was used with the modification that N_2 was substituted with O_2 as the circulating gas. With the gas loop closed, oxidation of SO_2 leads to a reduction in the total gas pressure following the consumption of oxygen. More oxygen was then let in at intervals to keep the total pressure constant within ± 0.02 bar. The SO_2 analysis followed the procedures described earlier for gases rich in SO_2 . The amount of oxidized SO_2 was found from the following formula, which also covers comparative experiments with sodium sulphite buffers:

$$\% \text{ oxidized} = \frac{n^{\circ} \text{start} - (n^{\circ} \text{end} + n_{SO_2, \text{gas}})}{n_{SO_2, \text{start}}} 100$$

where $n^{\circ} \text{start}$ = total no. of moles of S(IV)-compounds in the buffer at the start, $n^{\circ} \text{end}$ = do. at the end, $n_{SO_2, \text{gas}}$ = no. of moles of SO_2 present in the gas volume at the end and $n_{SO_2, \text{start}}$ = no. of moles of SO_2 added to the buffer before the start.

Reagents

These were p.a. reagents from Merck.

RESULTS

Gas-liquid equilibrium

Figure 4 shows gas-liquid equilibrium curves obtained for three different phosphate buffers B1, B2 and B3 at $55^{\circ}C$, all with the same start concentration of Na_2HPO_4 but with increasing concentration of NaH_2PO_4 . From these curves we infer:

- An increase in the NaH_2PO_4 -concentration causes $p_{SO_2}^*$ to increase. This may explain why addition of NaH_2PO_4 promotes the removal of SO_2 from the buffer during the evaporation-regeneration.
- The curves predict only a minor decrease in the cyclic capacity, $\Delta C_{SO_2}^0$, when more NaH_2PO_4 is added. As an example, when the buffers enter and leave the absorber with $p_{SO_2}^* = 5 \cdot 10^{-5}$ and $2 \cdot 10^{-3}$ bar, $\Delta C_{SO_2}^0 = 0.83, 0.78$ and 0.77 M for buffer B1, B2 and B3, respectively. $p_{SO_2}^* = 5 \cdot 10^{-5}$ bar is the value expected for the regenerated buffer B2 at $55^{\circ}C$ based on the result of the regeneration experiment reported below.

Figure 5 demonstrates the effect of absorption temperature on $p_{SO_2}^*$ for buffer B2. The curves indicate the following trend:

- Lowering T_A leads to an increase in absorption efficiency as well as in cyclic capacity. Again assuming $C_{SO_2}^0 = 0.58$ M in the regenerated buffer, the corresponding $p_{SO_2}^*$ -values are $8.1 \cdot 10^{-5}$, $5.0 \cdot 10^{-5}$ and $2.1 \cdot 10^{-5}$ at 70,

55 and 40°C, respectively. Parallel to this $\Delta C_{SO_2}^0$ will increase from 0.61 to 0.79 and 1.03 M, respectively, when $p_{SO_2} = 2 \cdot 10^{-3}$ bar in the buffer leaving the absorber.

Evaporation - regeneration

In regenerating the buffer by evaporation, reactions (2)-(4) are reversed, H_2O and SO_2 are driven off, and a dense liquid phase/slurry forms. The system showed very little tendency of incrusting the heating element.

In figure 6 $C_{SO_2}^0$ and S_v are plotted as function of the vapor sample number for one evaporation experiment carried out with buffer B2. $C_{SO_2}^0$ is the residual concentration of SO_2 in the evaporator, with respect to the total volume of buffer added. It is seen that $C_{SO_2}^0$ is reduced from 1.53 M in the feed to a final value of 0.58 M, corresponding to $\Delta C_{SO_2}^0 = 0.95$ M. From figure 5 it is seen that the $C_{SO_2}^0$ -values given correspond to $p_{SO_2} = 1.5 \cdot 10^{-3}$ (1.53 M SO_2) and $2.1 \cdot 10^{-5}$ bar (0.58 M SO_2) at 40°C. From this we conclude that it will be possible to meet very low emission limits with this buffer. S_v is seen to end at 11.0 g/g SO_2 in this case. Using double-effect evaporation this corresponds to about 6-7 g/g SO_2 .

The $C_{SO_2}^0$ - and S_v -values here reported are both quite high compared with the results obtained with some other phosphate buffers investigated. In a preliminary search for a more optimal buffer we have obtained results indicating $C_{SO_2}^0$ below 0.4 M and S_v around 9 g/g for single effect evaporation.

Oxidation of SO_2

For a phosphate buffer with start composition 3.00 M Na_2HPO_4 + 1.00 M NaH_2PO_4 + 0.50 M Na_2SO_4 + 1.50 M SO_2 , the following results were obtained in experiments carried out at 60°C:

Oxidation time, min.	30	60
% oxidation	0.9	0.9

The oxidation is here considered as insignificant. This result is supported by the observation that there was no reduction in the gas pressure over a considerable time period when the gas circulation loop was closed. Even though very small oxidation losses are expected with the phosphate buffer, some Na_2SO_4 will accumulate, for instance due to SO_2 in the flue gas. There will therefore be need for ways to remove Na_2SO_4 without losing a significant amount of buffer. A simple and proprietary method is available for this.

COMPARISON WITH EXISTING TECHNOLOGY

The leading SO_2 recovery process is currently the Wellman-Lord (WL) process. In this SO_2 is absorbed in an aqueous sodium sulfite solution. Thereby the sulfite ions are transformed into bisulfate. The solution is thermally regenerated, whereby H_2O + SO_2 evaporates and solid Na_2SO_3 precipitates. The crystals are redissolved in condensate/water to the appropriate concentration for a new absorption-regeneration cycle, etc.

A main advantage of the new phosphate process over the WL process would be that chemically stable phosphates replace the more reactive sulfite /bisulfite as the buffer: while negligible oxidation was found with the phosphate buffer, a comparative experiment with a sulfite buffer ($1.70 \text{ M Na}_2\text{SO}_3 + 0.50 \text{ M Na}_2\text{SO}_4 + 1.22 \text{ M SO}_2$) showed a rapid fall in the pressure and 8.7 and 23.1% oxidation losses after 30 and 60 minutes, respectively. Also, while the phosphate buffer showed very little tendency of forming deposits in the evaporation experiments, very heavy incrustation of the heating element occurred with the sulfite system. As to S_v , indications are that significant lower values are possible with the phosphate buffer.

STATE OF DEVELOPMENT

The studies so far has been confined to the laboratory scale. A number of buffer formulas have been included in the studies and preliminary absorption experiments have been carried out in order to verify the excellent absorption capabilities of the buffer.

The process is now ready for pilot plant testing, and industrial partners are approached with the aim of commercialization.

SUMMARY

SO_2 in flue gases may soon represent an important source of sulfur. The citrate and adipate absorption/steam stripping processes studied earlier are claimed to be very competitive for recovering SO_2 from gases relatively rich in SO_2 . A new sodium phosphate based absorption/evaporation process possess very promising properties:

- High absorption capacity in combination with very complete absorption
- Favorable energy (steam) requirement per ton SO_2
- Practically no oxidation losses
- Little or no burdensome incrustation in the evaporator system
- Easy removal of sodium sulfate.

The studies reported strongly suggest that the phosphate process will be competitive even for gases relatively lean in SO_2 such as occurring in fossile fired power plants.

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NOMENCLATURE

- $C_{SO_2}^0$ = total residual concentration of SO_2 , referred to the total buffer volume added to the evaporator, or: total concentration of SO_2 , $kmol/m^3$
- p = partial pressure, bar
- P = total pressure, bar
- ppmv = parts per million, volumetric S_v = specific steam requirement, tons/ton SO_2 or g/g SO_2
- T_A = absorber temperature, $^{\circ}C$
- $\Delta C_{SO_2}^0$ = cyclic capacity, $kmol/m^3$
- * = equilibrium.
- M = gmole/l

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DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

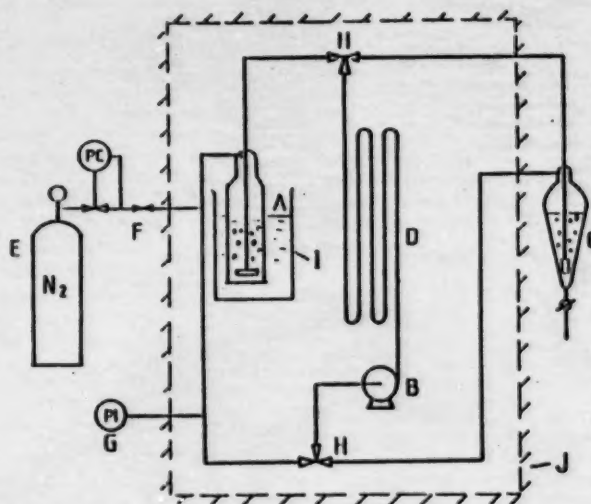


FIGURE 1. EQUIPMENT FOR GAS/LIQUID EQUILIBRIUM MEASUREMENT.

A = GAS WASHING BOTTLE WITH BUFFER SAMPLE, B = GAS PUMP, C = SEPARATION FUNNEL WITH H_2O_2 -SOLUTION, D = GLASS TUBE, E = N_2 CYLINDER, F, H = VALVES, G = MANOMETER, I, J = THERMOSTATED WATER BATH AND CHAMBER, PC = PRESSURE CONTROLLER.

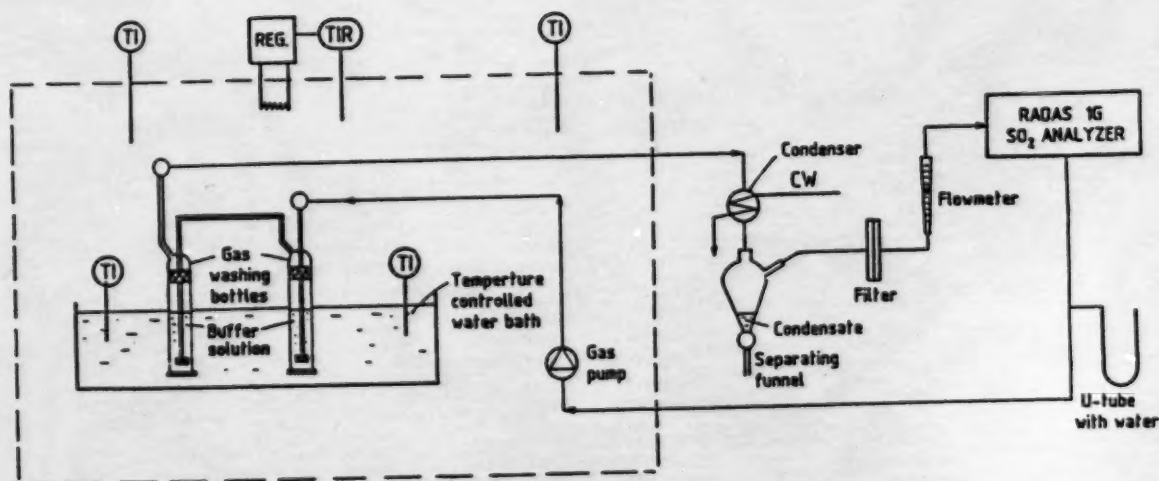


Figure 2 Modified gas/liquid equilibrium equipment.

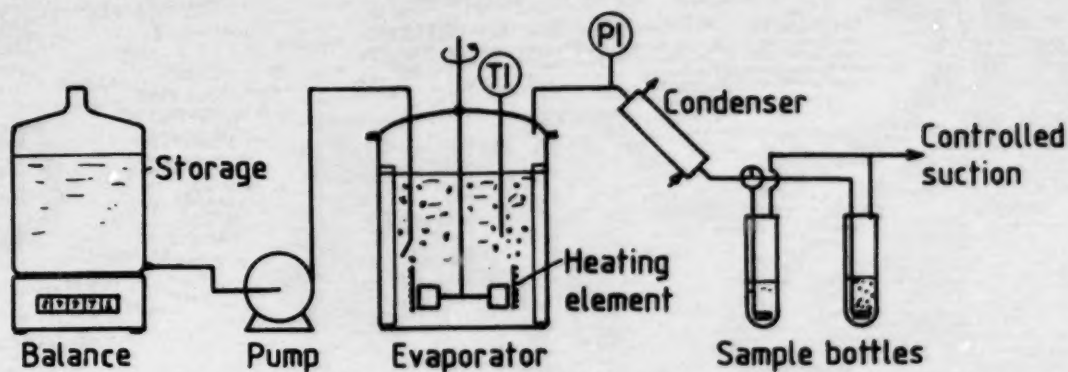
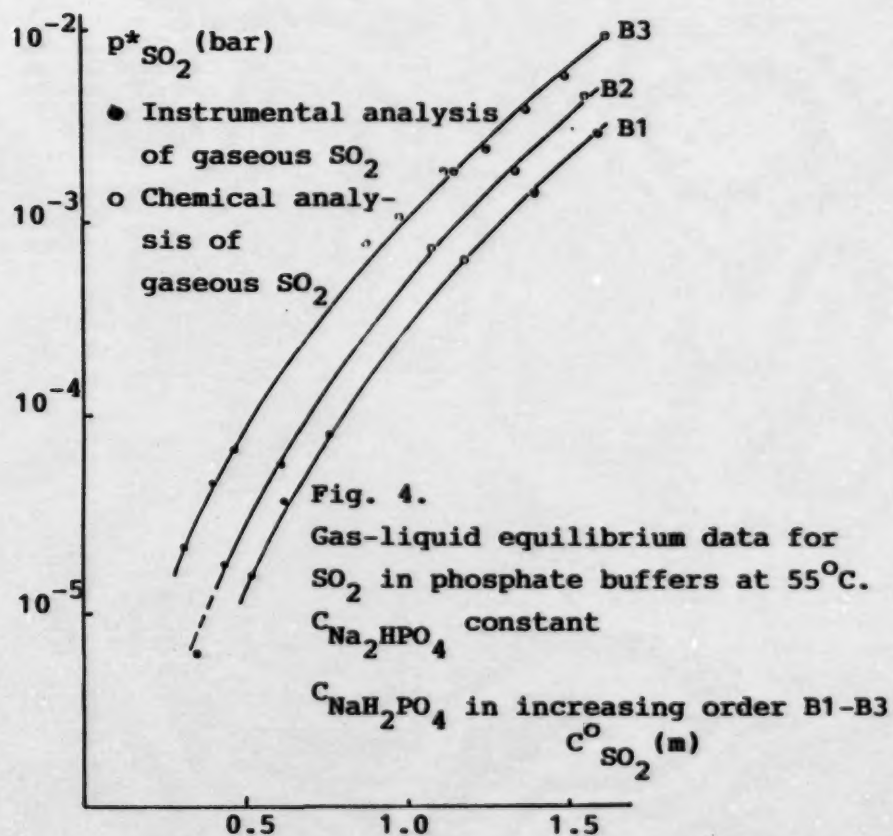


FIGURE 3. SIMPLIFIED FLOW DIAGRAM FOR THE EVAPORATION-REGENERATION EQUIPMENT.



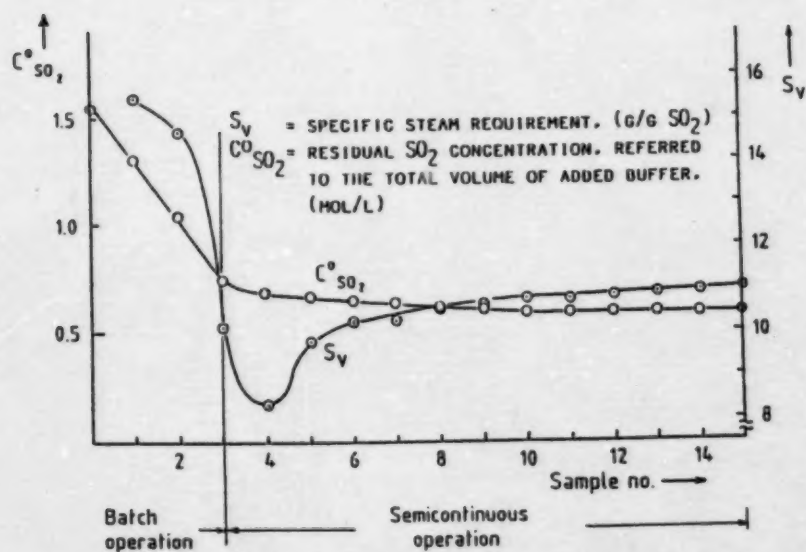
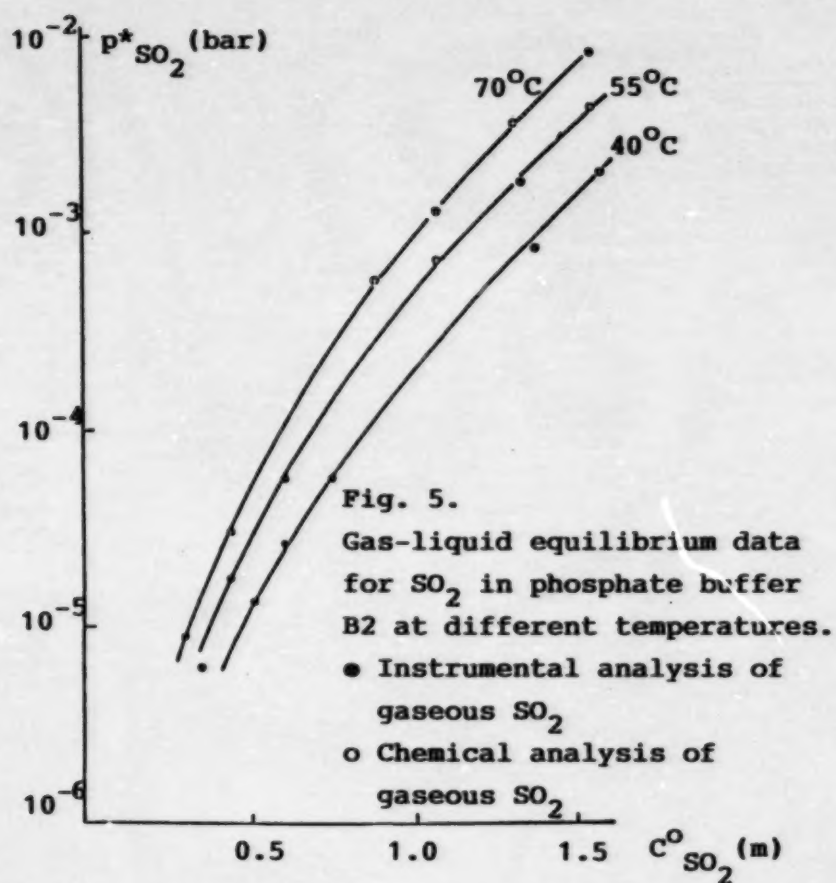


Fig. 6. EVAPORATION-REGENERATION DATA FOR PHOSPHATE
BUFFER B2 LOADED WITH SO_2 . ATMOSPHERIC PRES-
SURE.

THE 3 S - PROCESS:
SIMULTANEOUS (ACID GAS AND NO_x) SODIUM-BASED SORPTION OF
FLUE GASES

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ABSTRACT

This report deals with a new, totally dry additive process for simultaneous emission control of acid gases (SO₂, HCl etc.) AND NO_x as well as dust down to emission values usually only reached by wet or semi-dry processes.

The results secured so far come from mostly lab, some pilot-plant scale work employing sodium bi-carbonate and, at earlier stages, various other additives such as activated bauxite. If the promising results of desulphurisation greater than 95 %, de-chlorination greater 98 %, denoxing greater 80 % at additive stoichiometries ("NSR") substantially less than 1.5 can be proven on pilot scale, this dry 3S-process offers substantial economic advantages, especially for the retrofit scene.

BACKGROUND

Emission control processes employing the addition of dry, Ca- or Na-based pulverized additives without any addition of water or steam at any point from fuel input until stack have a long history (e.g. ref. 1). Our own experiences originate from pilot plant and large scale testing with calcium and sodium based additives beginning from about 1980 (ref. 2, 3) which resulted in a cooperative development and retrofit effort by ÖDK, Fläkt and Waagner-Biro for the 100 MW ÖDK P/S at Andrä/Austria in 1986 with the fullscale retrofit installation of a dry, 2-stage, 2-additive simultaneous dust and SO₂ emission control plant (FIG. 1, ref. 2, 4). With a normalized stoichiometric ratio (NSR) of 1.2 desulphurization of 80 %, with an NSR of 1.7 desulphurization of greater 90 % was proven and guaranteed. Raw gas SO₂-concentrations depend on the type of coal fired and run from about 1200 to over 5000 mg/Nm³.

Some observations were made during above mentioned large scale tests with sodium bi-carb which in due course could be matched-if not well understood - with information from published literature (ref. 5, 7, 8).

* Simultaneous denoxing in the order of about 10 % occurred, which by addition of various additional additives such as hart's horn salt NH₄HCO₃ and/or activated bauxite could be raised to approx. 50 %.

* Once the available NO_x-measuring instrumentation had been adapted to the presence of NH₃ (-compounds) and larger than the usual 5 %-contents of NO₂ in NO_x, it was secured that a varying percentage of NO to NO₂-conversion occurred after addition of sodium bi-carb which in turn results in visible, brownish plumes (ref. 5, among others). The visibility is in the order of 30 to 45 ppm NO₂ in the flue gas, depending on plume diameter PD, a general guideline given by ref. 6

$$\text{visual concentration } C_v = \frac{2100}{PD} ; C_v \text{ (vpm), PD (cm)}$$

* It was realised that lower reaction temperatures induced another inexplicable increase in SO₂- and NO_x-capture, cf. refs. 2, 3, 4, 7, 8.

Due to upcoming emission legislation which in local cases in Austria curbed NH₃-emission to a maximum of 3 vpm post-combustion tests with ammonia (-compounds) due to elevated NH₃-slip were discontinued.

FIRST BI-CARB LAB AND PILOT TESTS

Meanwhile-second quarter 1986-lab scale tests were in progress which showed for "typical cloth filter bicarb dust layers" the usual 80 % + desulphurization and up to about 80 % maximum denoxing with sodium bicarb with the simple drawback of quickly declining denoxing rates while high desulphurization was still achievable.

Scouting pilot scale tests (~ 500 m³/h) carried out at temperatures as low as 80° C in late 1986 and early 1987 confirmed prior lab results with respect to securing the "chemical possibility of denoxing beyond 66 %"(ref. 8) for extended periods (several hours) which in effect meant that-regardless of a high NSR at that time-it was in principle feasible to compete with other denoxing processes (e.g., SCR), even simultaneous ones such as electron beam processes. Denoxing means, indeed, the reduction of both: NO AND NO₂, NO₂-production staying below 20 - 40 vpm. NO_x-reduction, however, was strongly dependent on the incoming SO₂/NO_x ratio (cf. ref. 8), all other parameters being equal.

In another of our pilot plants HCl-containing waste-gases (~ 1500 m³/h) containing 1500 mg/Nm³ HCl and up were cleaned to below 30 mg/Nm³ HCl employing an NSR of around 1.5 (ref. 9), thereby securing a degree of dechlorination of more than 98 %.

FURTHER LAB TESTING

TEST PARAMETERS

Two general test rigs were experimented with on a bench scale:

fixed bed
fluidized bed

Of the varied experimental circuits employed one is shown in FIG. 2. Synthetic gas prepared by various gas mixing techniques was used in all cases, employing the following variations:

SO ₂	150 - 3000 vpm	NO _x	100 + 1200 vpm
SO ₂ /NO _x	1 - 6	O ₂	0 + 21 %
CO ₂	0 - 19 %	N ₂	remainder

Sorbents used (by itself and admixed) were: sodium bicarb, calcium hydroxide, activated bauxite which were employed on a oncethru basis, but also with semi-discontinuous feed. Reactor temperatures varied from 80 to 160° C.

Across the reactor SO₂, NO and NO₂ were measured and recorded continuously during all tests as well as pressure-difference Delta p. O₂ was recorded continuously during all tests, CO₂ in some cases as well as N₂O and SO₃. Calibration checks were made usually before and after tests and in some cases during tests runs to assure proper functioning. Tests ran from several hours to as long as 160 hours continuously. In addition to gas measuring analysis chemical analyses of the formed products were carried out after several crucial tests runs.

RESULTS FOR SODIUM BI-CARBONATE

- * ETA NO_x larger 80 %, ETA SO₂ larger 95 % with a stoichiometric ratio of less than 1.1 *) (relating to sorbent usage exceeding 90 %) when employing SO₂/NO_x ratios of 2 or larger
- * ETA NO_x reaches a max. of about 50 % for SO₂/NO_x = 1
- * NO₂-emission stays below 20 vpm
- * SO₂- and NO_x-sorption in gas as indicated by gas analyzing set-up (difference incoming - outgoing) relate to product analyses better than 85 to 95 %
- * SO₂ is reacted to solely sodium-sulfate, NO_x solely to sodium nitrate (practically no sulfites or nitrites)
- * Sharp decline in desulphurization and denoxing occurs when the O₂-concentration drops to below about 3 %
- * ETA NO_x and ETA SO₂ increases with increasing contact time towards an upper level
- * ETA NO_x (FIG. 3) and ETA SO₂ increases with decreasing gas velocity
- * No additional N₂O or SO₃ originates from the reaction

*) Na/S ≡ 1 for every 2 moles of NaHCO₃ consumed by 1 mole of SO₂,
 Na/NO ≡ 1 for every 1 mole of NaHCO₃ consumed by 1 mole of NO

* For optimum results a temperature window of about $\pm 15^{\circ} \text{C}$ should be observed

* Delta p across the reactor varied from 100 to 600 mm WG depending on the type of bed used

ECONOMICS

We have done some calculations which we believe to be correct for central European conditions (FIG. 4) thereby comparing capital and proportional costs of the 3S-process with a combination of state-of-the-art wet FGD plus additional SCR denoxing plant.

We realize that the situation in the US may be vastly different, thereby even improving the odds for the 3S-process since we expect from some comments that nahcolite may be available at rather less than AS 3000/ton (equivalent to roughly US Dollar 230,-/ton). Furthermore we expect from further comments (ref. 10) that disposal of water soluble salt containing ashes may substantially cost less than the calculated AS 2000,-/ton (roughly equivalent to US Dollar 150/t).

We welcome, however, any comments and critical remarks with respect to the applicability of this process to the US retrofit situation.

FURTHER PLANS

A new pilot test rig is right now in the final planning stage allowing the optimization of the size of the reactor as well as securing the higher than 90 % usage of sodium bi-carb indicated by lab work so far.

Of the many recycling suggestions and recycling projects tried (e.g. ref. 11) apparently none so far have reached a large-scale technical nor commercially competitive status. Further thought should be given to improved recycling or elution-proof disposal techniques, for this would, indeed, increase the applicability of sodium-based processes remarkably.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred

ACKNOWLEDGEMENTS

FIG. 1 is the result of a cooperative development effort of ÖDK Österreichische Draukraftwerke AG of Austria, Svenska Fläkt and Waagner-Biro AG.

Lab and pilot test work (Project number 3/5660) is partially funded and supported by the Forschungsförderungsfonds für die gewerbliche Wirtschaft, DI. Doris Pllak being the Project Officer.

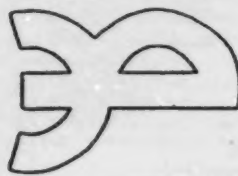
Cordial thanks are extended to Dr. George R. Offen of EPRI for offering and accepting this paper and presentation suggested by us at rather a late date.

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DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.



Simultane Trockenadditiv-Schadstoffabscheidung Dry-additive-injection for simultaneous emission control

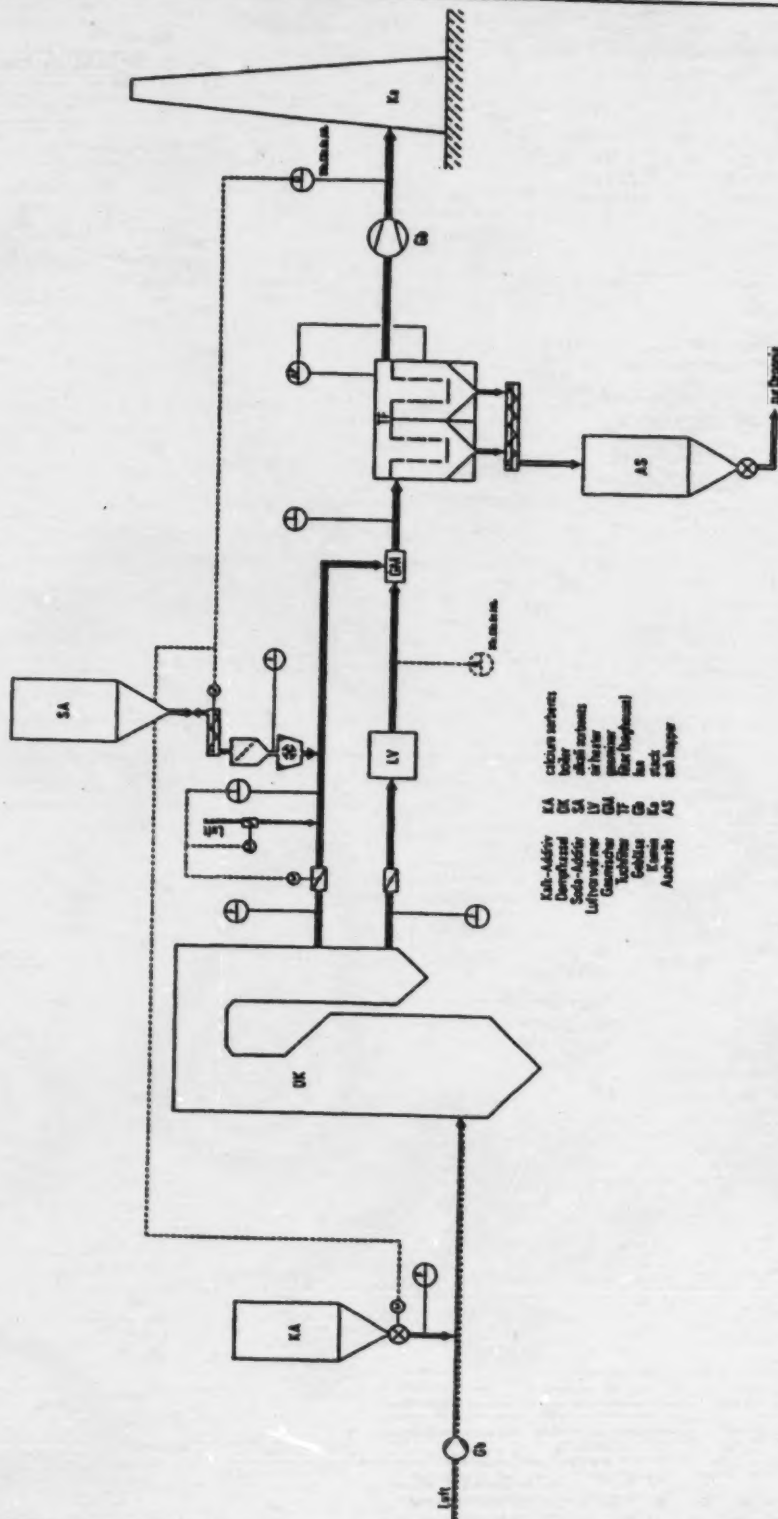


FIG. 1 100 MW_e 2-Stage, Dry Additive SO₂ and Dust Retrofit Emission Control
 Installed and operated at St. Andrä/Austria since 1986

WAAGNER-BIRÓ
 ANTONKREUZBURG

TECHNOLOGY FOR A BETTER TOMORROW

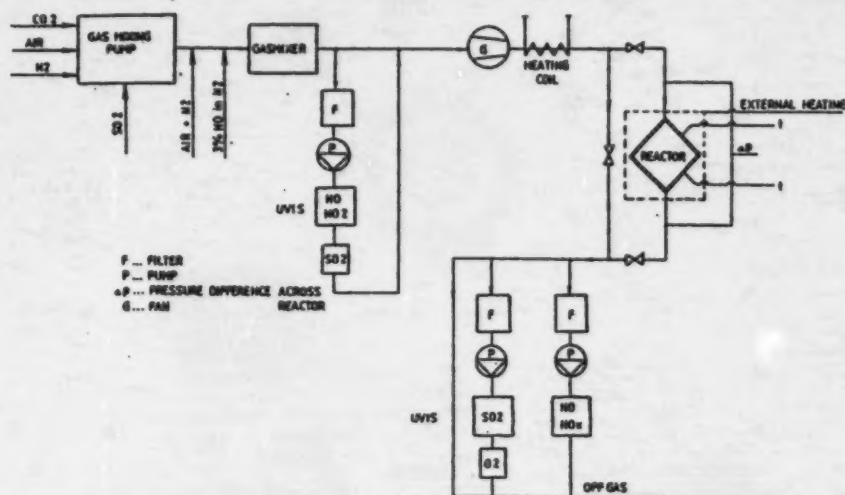


FIG. 2 Experimental lab-scale test set-up

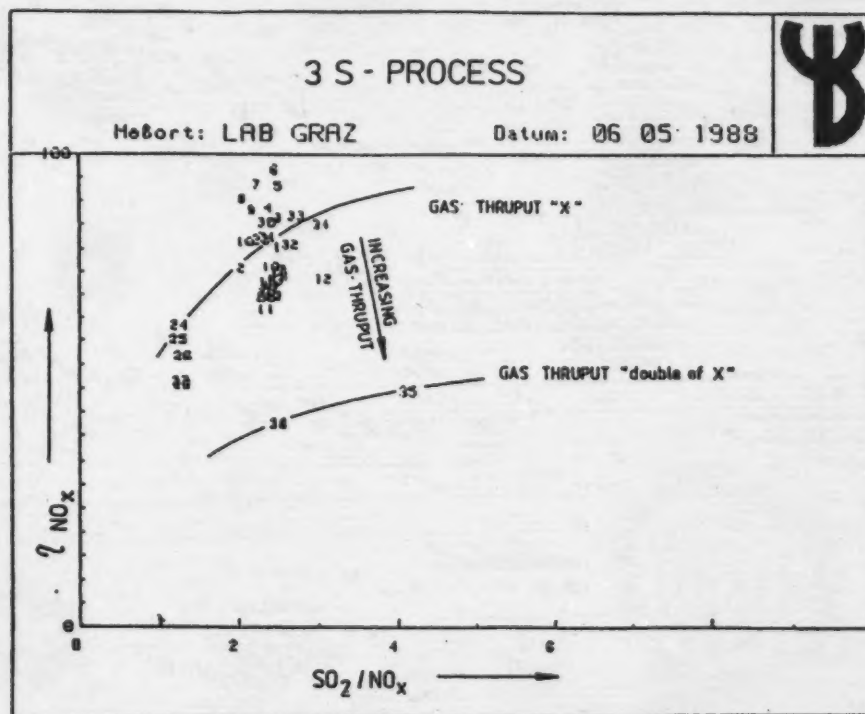
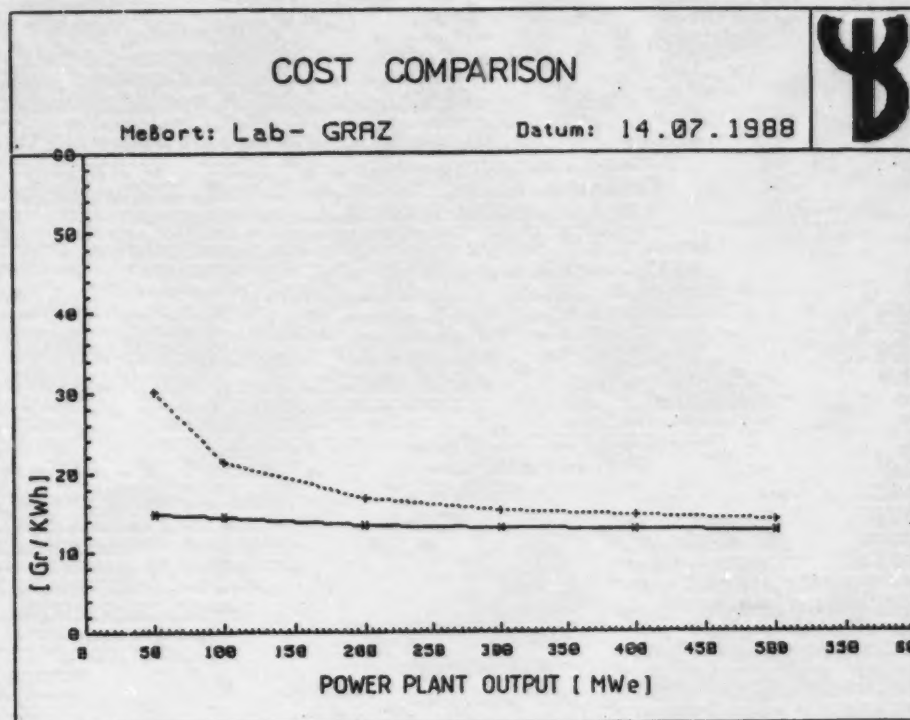


FIG. 3 Denoxing as function of gas thru-put (lab scale) and incoming SO_2/NO_x

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TOTAL COST 3S+DISP [Gr/KWh]^{a)} * — * — * — *

TOTAL COST WET FGD+ SCR [Gr/KWh]^{a)} + ... + ... + ... + ...

a)
1Gr ≡ 0.01 AS
13 AS ≡ 1 US \$

BASIS OF CALCULATION:

NO_x incoming.....600 mg/Nm³
 NO_x emitted.....100 mg/Nm³
 SO₂ incoming.....2000 mg/Nm³
 SO₂ emitted.....200 mg/Nm³
 Capitalization
 of P.C.I. 18.5 %
 price sodium
 bi-carbonate....2000.- AS/t
 price CaCO₃.....350.- AS/t
 price ammonia.....6.- AS/kg
 bi-carb stoich.
 ratio.....1.1
 annual hours
 of operation....4000 h/a
 disposal costs..2000 AS/t
 delta p reactor.2000 Pascal

FIG. 4 Total Costs (Investment plus Proportional) Compared: 3 S-Process vs. Wet FGD + SCR

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TECHNOLOGY FOR A BETTER TOMORROW

**PRODUCTION OF LIME/FLY ASH ABSORBENTS
FOR
FLUE GAS DESULFURIZATION**

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ABSTRACT

Previous workers have shown that fly ash can be reacted with $\text{Ca}(\text{OH})_2$ to produce solids which are very reactive towards SO_2 at bag filter conditions. The present study fundamentally investigates the important parameters of the fly ash- $\text{Ca}(\text{OH})_2$ reaction. The dissolution rate of fly ash, thought to be the rate limiting step of the overall reaction, was determined to depend on the fly ash type and on the pH of the slurry. It is shown that high calcium fly ashes dissolve faster than do low calcium fly ashes and that the dissolution rate for both types of fly ash increased with slurry pH. A new "selective dissolution" method was formulated to determine the composition of the reactive surface layer of the fly ash- $\text{Ca}(\text{OH})_2$ reaction products. This method allows one to determine the conversion of the silica in the reaction products. This conversion data was correlated with the ability of the reaction product to remove SO_2 in a packed bed reactor that was designed to simulate bag filter conditions.

INTRODUCTION

Two important dry processes for flue gas desulfurization (FGD) utilize spray drying of Ca(OH)_2 and the injection of dry, calcium-based sorbent into humidified gas at 60-100 °C (1). In both of these technologies, gas/solid reaction makes a major contribution to SO_2 removal both in the ductwork and in the particulate removal device, especially if a bag filter is used. The pozzolanic reaction of fly ash with Ca(OH)_2 to produce reactive solids for use in these processes has been investigated up to the pilot plant scale (2,3,4,5,6). This pozzolanic reaction has primary importance in the chemistry of cement. The use of fly ash as a reagent material for the production of reactive solids for FGD is very attractive, both economically and environmentally, because fly ash is a waste product from all coal fired power plants.

Jozewicz (2) studied the reaction of fly ash with Ca(OH)_2 to produce reactive solids for use in FGD. In bench-scale experiments using a packed bed reactor, Jozewicz found that the solids produced by slurrying fly ash with Ca(OH)_2 were much more reactive towards SO_2 than was Ca(OH)_2 . He found that increasing the fly ash loading from 0.5 to 20 g fly ash/g Ca(OH)_2 increased the Ca(OH)_2 utilization from 17 to 78%. Jozewicz also found that silica was the most reactive component of the fly ash and that the solids reactivity increased with slurry time and slurry temperature. Jozewicz postulated that the rate limiting step of the reaction of fly ash with Ca(OH)_2 was the dissolution of silica from the fly ash.

In order to increase the reaction rate between fly ash and Ca(OH)_2 , several researchers have tested additives to the fly ash- Ca(OH)_2 slurries in an attempt to increase the dissolution rate of silica from the fly ash. Since fly ash is primarily a glassy substance, and since it is well known that NaOH etches glass, Chu (3) tested the addition of NaOH to the fly ash- Ca(OH)_2 slurries in order to enhance the reaction of fly ash with Ca(OH)_2 . The addition of 0.08 M NaOH to the fly ash - Ca(OH)_2 slurry increased the reactivity of the product solids towards SO_2 from 18 to 65 moles of SO_2 removed/100 moles of Ca(OH)_2 . The addition of 0.08 M NaOH to the slurry also increased the reactivity of the product solids towards NO_x from 1 to 4 moles NO_x removed/100 mole Ca(OH)_2 . Phosphoric acid and ammonium phosphate have also been tested as additives for fly ash dissolution, and similar increases in the product solids reactivity were reported (4).

An alternative way to increase the reaction of silica with Ca(OH)_2 is to use a more reactive form of silica. Jozewicz and Chang (4) have tested diatomaceous earth as a source of silica for the production of reactive solids for use in dry FGD systems. This naturally occurring substance is composed of essentially pure amorphous silica. Although diatomaceous earth was shown to be much more reactive than fly ash, the most likely source for silica comes from the power plant fly ashes, since the cost of the alternate sources of silica would be much higher than that of fly ash. An interesting observation made by Jozewicz et al. (5) was that the optimum molar ratio of diatomaceous earth: Ca(OH)_2 was 1:1 for the production of solids that are reactive towards SO_2 .

The presence of an optimum ratio of SiO_2 : CaO in the solids produced by slurrying fly ash with Ca(OH)_2 has been postulated. Peterson and Rochelle (6) found that the solids formed in slurries containing from 10 to 100 ppm of dissolved calcium were more reactive towards SO_2 than the solids formed in solutions containing lesser or greater amounts of dissolved calcium. They attributed this effect to the changing ratio of SiO_2 : CaO of the product solids. In experiments using reagent silica and Ca(OH)_2 , this ratio has been shown to depend on the dissolved calcium concentration in the solution (7,8).

Jozewicz et al., (9) investigated the effects of pressure hydration on the reactivity of the fly ash- Ca(OH)_2 solids towards SO_2 . The purpose of these experiments was to increase the fly ash dissolution rate by increasing the slurry temperature. Jozewicz et al. found that there is an optimum slurry temperature between 110 and 160 °C, and indicated that there are two factors necessary for a sorbent to readily react with SO_2 : large sorbent surface area and amorphous surface structure. The requirement of the presence of an amorphous surface layer may be related to the presence of an optimal ratio of SiO_2 : CaO in the surface layer of the solids.

The use of the fly ash-based sorbents has been successfully demonstrated on a larger scale (5,10). In pilot plant experiments with duct injection systems, the utilization of Ca(OH)_2 was 25 to 35% higher when solids produced by slurrying fly ash with Ca(OH)_2 were used instead of hydrated lime. However, the single pass conversion of the reagent was only 30 to 50%, so recycle of the solids from the particulate control device is mandated. The recycle of spent solids introduces a new variable in the production of reactive solids, since there will be significant amounts of CaSO_3 present in the recycle stream. The effect of the presence of CaSO_3 in the slurry on the reactivity of the solids produced in those slurries remains to be quantified.

SCOPE OF WORK.

The scope of this work was to determine the $\text{SiO}_2:\text{CaO}$ ratio on the surface layer of the fly ash- Ca(OH)_2 products, to determine which of these products are most reactive towards SO_2 , and to determine which parameters are most important for the production of these solids. This was accomplished by slurrying fly ash with Ca(OH)_2 under a variety of slurrying conditions and testing the product solids for reactivity towards SO_2 . Fly ash dissolution experiments were also performed to investigate the effects of slurrying conditions on the dissolution rate of fly ash in the absence of reaction with Ca(OH)_2 . This study investigated the effects of slurry temperature, slurry time, fly ash type, CaSO_3 loading, and NaOH concentration on the reaction rate.

EXPERIMENTAL APPARATUS AND PROCEDURE

FLY ASH DISSOLUTION

Fly ash dissolution experiments were performed in a temperature controlled, 500 ml stainless steel autoclave. 500 mg of fly ash was added to 400 ml of distilled water containing 2 g of Na_2EDTA /400 ml H_2O . The EDTA was added to complex the calcium which dissolves from the fly ash so as to prohibit the precipitation of calcium silicates from the solution. The NaOH concentration was adjusted with 5 N NaOH before the addition of the fly ash to the solution. The NaOH concentration was varied from 0.0 to 0.5 M and the slurry temperature was varied from 25 to 90 °C. The solutions were stirred at 1000 rpm for up to 24 hours as the fly ash dissolved. Five types of fly ash, ranging from 4 to 30% CaO (Table 1), were used in the experiments.

Solution samples were taken with time and filtered with a 0.45 micron filter. The filtrates were analyzed for silicon and aluminum using atomic absorption spectrophotometry (AA). The conversion of the metals in the fly ash was determined by dividing the measured concentration of the metals in solution by the calculated concentration for total dissolution of the fly ash (based on the chemical analyses presented in Table 1).

SOLIDS REACTIVITY

The overall experimental procedure for the determination of the solids reactivity involved three types of experiments: solids preparation; solids reactivity; and selective dissolution of the reactive solids. The procedure is more easily understood if these experiments are described separately.

Solids Preparation.

Reacted solids were prepared by slurrying fly ash with Ca(OH)_2 in the same autoclave used for the fly ash dissolution experiments. In the base case slurry conditions, 35 grams of Ca(OH)_2 (Fisher Scientific) was slurried with 105 grams of fly ash in 400 ml of distilled water. The NaOH concentration in the slurry was adjusted before reagent addition using 5 N NaOH . The reagent Ca(OH)_2 was added before the fly ash to allow for complete saturation with Ca(OH)_2 . After 15 minutes the fly ash was added, normally at a loading of 3 g fly ash/g Ca(OH)_2 . Two types of fly ash, Clinch River and Fayette,

were used in the reactivity experiments (Table 1). The slurry temperature was varied from 65 to 160 °C and the stirring speed was 1000 rpm. The NaOH concentration was varied from 0.0 to 0.3 M.

Slurry samples were taken every hour for 8 hours. The samples were vacuum filtered and the solids were oven dried for 1 hour at 110 °C. These dry solids were later used in the solids reactivity and solids conversion tests. The filtrates were filtered with a 0.45 micron filter and cooled to room temperature. The pH of the filtrates was measured at room temperature and the dissolved metal concentrations were determined using atomic absorption spectroscopy.

Solids Reactivity

The solids reactivity experiments were conducted in a packed bed reactor (Figure 1) designed to simulate bag filter conditions (3). The pyrex reactor (4 cm in diameter and 12 cm in height) was immersed in a water bath where the temperature was controlled to within 1 °C. Flue gas was synthesized by combining N₂, CO₂, and SO₂ from gas cylinders with house air. Water was added to the system by sparging the nitrogen stream through distilled water at the reaction temperature.

The reactor was equipped with a bypass to allow for preconditioning of the solids and to allow the gas concentration to stabilize before starting the experiment. After the reactor, the gas was cooled and the water condensed out by an ice water condenser. The dry gas was sent to a pulsed fluorescent SO₂ analyzer (Thermo-Electron Series 40). The SO₂ concentration was continuously recorded and the concentration curve was integrated to determine solids reactivity.

The reactivity of the sorbents towards SO₂ is expressed here as "Ca(OH)₂ conversion". Ca(OH)₂ conversion is defined as the total number of moles of SO₂ removed after 1 hour divided by the initial number of moles of Ca(OH)₂ in the sorbent.

The experimental conditions for the packed bed reactor system were chosen to simulate conditions of a fabric filter downstream from a coolside dry FGD process. The synthetic flue gas flow rate was 4.6 l/min (0 °C, 101 KPa) with 7% O₂, 10% CO₂, 12 % H₂O, and the balance nitrogen. The reactor temperature was 66 °C and the SO₂ concentration was 450 to 550 ppm. The relative humidity of the gas was 51%.

The solids loading in the reactor was typically 0.4 g of Ca(OH)₂ with 1.2 g of fly ash. The amount of material placed in the reactor was adjusted so that the Ca(OH)₂ loading was always 0.4 grams. The reagent was sieved through a 115 mesh screen and dispersed in 40 g of 100 mesh (average) silica sand to avoid channeling caused by Ca(OH)₂ agglomeration (11). Before each experiment the solids were preconditioned at 85% relative humidity (2.6 l/min N₂ at 66 °C) for 8 minutes and for 10 more minutes at 51% relative humidity (4.6 l/min N₂ at 66 °C). After this preconditioning, the solids were exposed to the synthetic flue gas for 1 hour.

Selective Dissolution Experiments

The compositions of the reactive, calcium silicate surface layer on the fly ash-Ca(OH)₂ reaction products were determined by selectively dissolving the surface layer while leaving the unreacted fly ash core intact. This was accomplished by adding 200 mg of the solids to 100 ml of 0.1 M HCl. The mixture was stirred with a magnetic stirrer for 5 minutes at room temperature. An aliquot of the mixture was taken and filtered with a 0.45 micron membrane filter. The filtrate was analyzed for aluminum, silicon, and calcium concentrations using atomic absorption spectrophotometry.

The composition of the reactive surface layer was approximated by the molar ratio of calcium to silicon and aluminum in the filtrate solution. The conversion of the metals in the fly ash was determined by dividing the measured concentration of the metals in filtrate solution by the calculated concentration for total dissolution of the fly ash (based on the chemical analyses presented in Table 1).

RESULTS

FLY ASH DISSOLUTION

From a review of the literature concerning the use of fly ash in concrete, it is clearly evident that some fly ashes perform much better than do others. The reason for this difference is generally attributed to the difference in the availability of silica from the fly ash. To determine this availability, several wet chemistry techniques have been proposed.

The Raask test (12) determines the availability of the silica by stirring 150 mg of fly ash in 0.1 M HF and then monitoring the conductivity of the solution. This test has been criticized due to the assumption that the increase in conductivity is due only to the dissolution of silica from the fly ash. Most fly ashes, especially high calcium fly ashes, contain materials that will dissolve easily (e.g. Ca, Na, K) and will therefore increase the conductivity of the solution and give artificially high silica dissolution rates.

Another test, proposed by Cabrera, et al., (13) involves repeatedly boiling and cooling a mixture of fly ash and 5 M NaOH and determining the amount of silica and aluminum that dissolve from the fly ash. This test also has shortcomings since no effort was made to avoid precipitation of calcium silicates on the surface of the fly ash particles due to the reaction of the calcium with the silica present in the fly ash. This precipitation would lead to a lower rate of silica dissolution from the fly ash due to the removal of silica from the precipitation of calcium silicates and due to the increased mass transfer resistance of the product calcium silicate layer on the surface of the fly ash.

Since the rate of dissolution of silica from the fly ash is thought to limit the overall rate of fly ash- $\text{Ca}(\text{OH})_2$ production, the dissolution rate of fly ash was studied in the absence of the precipitation reaction of calcium silicates. This was accomplished by adding EDTA to the solution to complex the calcium that dissolves from the fly ash, so as to avoid the precipitation of calcium silicates.

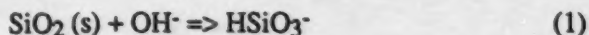
Effect of NaOH concentration

It has been shown that the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids towards SO_2 can be improved by the addition of NaOH to the fly ash- $\text{Ca}(\text{OH})_2$ slurry (3,4,5,6). The NaOH supposedly increases the dissolution rate of the fly ash and therefore increases the reaction rate of the silica from the fly ash with the $\text{Ca}(\text{OH})_2$ in solution. Fly ash dissolution experiments were performed to quantify the effect of the NaOH on the dissolution rate of the fly ash.

The effect of NaOH concentration on the dissolution rate of fly ash was investigated using Clinch River fly ash slurried at 90 °C. The NaOH concentration in the solution was varied from 0.0 to 0.5 M and the rate of fly ash dissolution was determined by monitoring the solution for dissolved silicon and aluminum metals. The results from these experiments are shown in Figures 2,3, and 4.

Figure 2 shows the effect of NaOH concentration on the conversion rate of silicon from the fly ash. The data show that the conversion increases with slurry time and with NaOH concentration. The figure shows the conversion of the silicon in the fly ash versus a reduced time. The reduced time is defined here as the time of dissolution divided by the time to 20% conversion (t_{20}) of the silicon in the fly ash. As Figure 2 shows, plotting the data this way collapses all of the data from the dissolution experiments onto the same curve. Since all of the data collapse, it is possible to determine the order of reaction with respect to the hydroxide concentration by plotting $1/t_{20}$ versus the concentration of NaOH in the slurry on a log-log graph. Figure 3 shows that the dissolution of silica from the fly ash has a reaction order of 1.1 with respect to hydroxide.

The dissolution rate of silica from the fly ash increases with NaOH concentration because silica is more soluble at high pH (14) and because the reaction for silica dissolution can be written as :



The dissolution rate of aluminum was also found to increase with NaOH concentration in the slurry. Figure 4 shows that for low silicon conversions, the conversion of the aluminum in the fly ash was higher than the conversion of silicon in the fly ash, but for high silicon conversions, the conversion of the aluminum was lower than the conversion of the silicon. This indicates that the dissolution of aluminum from the fly ash is not as dependent on the hydroxide concentration as is the dissolution of silicon from the fly ash. Through an analysis similar to that of the data for silicon conversion, Figure 3 shows that the reaction order of aluminum dissolution with respect to hydroxide is only 0.83.

Effect of Temperature

Clinch River fly ash was selected to determine the effect of slurry temperature on the dissolution rate of fly ash. The ash was slurried in 0.1 M NaOH at slurry temperatures from 25 to 90 °C. The dissolution rate was determined by monitoring the solution for dissolved silicon and aluminum using atomic absorption spectrophotometry. The data are presented in Figure 5.

Figure 5 shows that the dissolution rate of silicon from the fly ash is a strong function of the slurry temperature. The activation energy was determined to be 19.3 kcal/mol.

Effect of Fly Ash Type

Most of the previous investigations of the reaction of fly ash with Ca(OH)_2 to produce solids for use in FGD were performed using low calcium fly ashes (3,4,5). A significant fraction of the fly ashes produced in the USA are high calcium fly ashes, however, and these ashes seem to be more beneficial for the production of solids for use in FGD because some of the calcium present in the fly ash can be utilized to produce solids for FGD (6,15). For this reason, the present investigation encompasses a variety of fly ashes.

Five different fly ashes were used to determine the effect of fly ash type on the dissolution rate of the fly ash. These ashes included two low calcium fly ashes and three high calcium fly ashes (Table 1). The fly ashes were slurried at 90 °C in 0.1 M NaOH for up to 6 hours. The conversion of the fly ashes was determined by analyzing the solution for dissolved aluminum and silicon. The results from these experiments are shown in Figure 6.

Figure 6 shows the effect of fly ash type on the dissolution rate of aluminum from the fly ash. The data show that the initial dissolution rate of the fly ash is a strong function of the fly ash type. A large portion of the high calcium fly ashes dissolves almost instantaneously while the low calcium fly ashes dissolve more slowly. Similar effects were observed for the dissolution rate of silicon from the fly ash, although not to the same degree (not shown). This suggests that there is some very reactive material in the high calcium fly ash which is not present in the low calcium fly ash. It is therefore assumed that the high calcium fly ashes are more reactive towards Ca(OH)_2 and therefore would be more beneficial than low calcium fly ashes for producing solids for flue gas desulfurization.

The presence of highly reactive forms of aluminum and silicon in the high calcium fly ash agrees with the observations of Diamond (16) which showed that high calcium fly ashes contain a highly reactive, calcium-aluminate-silicate species that is not found in low calcium fly ash. He indicates that this species is probably $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ with inclusions of SiO_2 . It is probably this species which makes the dissolution of high calcium fly ash so much different from the low calcium fly ash.

REACTION OF FLY ASH WITH Ca(OH)_2

Effect of Additives/Slurry Conditions

A number of previous studies (2,3,4,5,6) have shown that the reactivity of the fly ash- Ca(OH)_2 solids towards SO_2 is a function of the slurry time, the slurry temperature, the fly ash: Ca(OH)_2 ratio, and the presence of additives to the slurry to increase the fly ash dissolution rate. The fly ash- Ca(OH)_2 reaction experiments reported here duplicated much of this work in order to produce solids that could be tested with the selective dissolution method. The results from these tests were correlated with the sand bed reactor tests.

To determine the effect of slurring conditions on the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids towards SO_2 , Clinch River fly ash was slurried with $\text{Ca}(\text{OH})_2$ under a variety of slurring conditions. The solids produced in these slurries were dried and tested for reactivity towards SO_2 and for product composition using the selective dissolution method. Some of the results are shown in Figure 7 and all results are tabulated in Table 2.

Figure 7 shows that the addition of small amounts of NaOH to the fly ash- $\text{Ca}(\text{OH})_2$ slurries increases the reactivity of the product solids towards SO_2 for short slurry times (<10 hr), but for longer slurry times the NaOH is less beneficial or even detrimental for solids reactivity. The data also show that the reactivity of the solids produced in 0.30 M NaOH are less reactive than the solids produced in 0.18 M NaOH even though the fly ash: $\text{Ca}(\text{OH})_2$ ratio is higher in the former solids (higher ratios favor solids reactivity when no NaOH is present in the slurry). This effect has been observed before (6) and indicates that the solid phases formed in slurries containing large amounts of NaOH are different from those formed in slurries containing no or small amounts of NaOH.

The data from Table 2 show that the slurry conditions have a strong effect on the reactivity of the solids towards SO_2 . The data also show that the slurry conditions have a strong effect on the ratio of SiO_2 :CaO on the surface of the solids as determined by the selective dissolution method. The data show that this ratio generally increases with slurry time, slurry temperature, NaOH concentration, and fly ash: $\text{Ca}(\text{OH})_2$ ratio.

Effect of Fly Ash Type

Since the fly ash dissolution experiments showed that all of the high calcium fly ashes behaved similarly and differently than the low calcium fly ashes, the fly ash- $\text{Ca}(\text{OH})_2$ reaction experiments were conducted with one fly ash from each type. Clinch River fly ash was selected to represent the low calcium fly ashes, and Fayette fly ash was selected to represent the high calcium fly ashes.

The fly ashes were slurried with $\text{Ca}(\text{OH})_2$ at 90°C for up to 9 hours at a ratio of fly ash to $\text{Ca}(\text{OH})_2$ of 3:1. The solids produced in these slurries were dried and tested for reactivity towards SO_2 . The composition of the solids and the total conversion of the fly ash were determined by the selective dissolution method. The results are shown in Figure 8 and are listed in Table 2.

The data in Table 2 show that the solids prepared using the high calcium fly ash are more reactive towards SO_2 than are the solids prepared with the low calcium fly ash. A fraction of the increase in reactivity of the high calcium fly ash solids arises from the high alkalinity of this fly ash. That is, some of the calcium from the fly ash reacts with the SO_2 to give an artificially high $\text{Ca}(\text{OH})_2$ conversion. The data in Table 2 are corrected for this effect by using the data from the selective dissolution method to determine how much of the calcium in the high calcium fly ash is converted to products that are able to react with SO_2 . However, the data in Table 2 indicates that the solids produced using the high calcium fly ash are more reactive than the solids produced using the low calcium fly ash even when the solids reactivity data are corrected for this increase in calcium content of the solids.

Another reason for the greater reactivity of the solids formed from the high calcium fly ash can be explained by the greater availability of silica from this ash. Figure 8 shows the results from the fly ash dissolution experiments along with the data from the selective dissolution experiments for the low- and high-calcium fly ash- $\text{Ca}(\text{OH})_2$ solids. The data show that the silica present in the high calcium fly ash is much more reactive than the silica present in the low calcium fly ash. This is another major reason for the increased reactivity of the high calcium fly ash towards SO_2 - the degree of calcium silicate production is higher for the high calcium fly ash. These high surface area calcium silicates are very reactive towards SO_2 .

Figure 8 also compares the rate of silicon conversion for the fly ash dissolution experiments (where no precipitation occurs) with the rate for the fly ash/ $\text{Ca}(\text{OH})_2$ reaction experiments (where a significant product layer is precipitated on the surface of the fly ash particle). The data show that there is a large depression in the silicon conversion rate of the fly ash when the precipitation is allowed to occur. This depression is probably due to an increase in the mass transfer resistance when the product layer is present on the surface of the fly ash.

Effect of CaSO₃

In a low temperature duct injection/baghouse pilot plant system, it was found that the conversion of the $\text{Ca}(\text{OH})_2$ in the fly ash/ $\text{Ca}(\text{OH})_2$ solids was low (35-50%) for a single pass of the solids through the system (5). This indicates that recycle of the solids must be employed to achieve acceptable reagent conversion. If recycle matter is present in the slurry, there will be significant amounts of CaSO_3 present in the slurry. The effect of the presence of CaSO_3 on the reactivity of the solids produced in the slurries has not been fully investigated.

Jozewicz and Rochelle (2) found that the presence of CaSO_3 in the fly ash slurry leads to the formation of long crystals that are calcium-alumino-sulfite materials that are similar to ettringite ($\text{Ca}(\text{Al}(\text{OH})_6)_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$). They found that the reactivity of the solids produced in slurries containing large amounts of CaSO_3 were more reactive towards SO_2 than solids formed in slurries containing no CaSO_3 . However, the solids formed in the presence of small amounts of CaSO_3 were less reactive than the solids formed in slurries containing no CaSO_3 .

Chu and Rochelle (3) found no effect of CaSO_3 on the reactivity of the solids towards SO_2 , but found a strong beneficial effect on the solids reactivity towards NO_x . Peterson and Rochelle (6) found that the presence of CaSO_3 had only a slight beneficial effect on the solids reactivity when no NaOH was present in the slurry, but the CaSO_3 had a large, beneficial effect on the solids reactivity when NaOH was present in the slurry.

Laboratory produced $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ was slurried with Clinch River fly ash and $\text{Ca}(\text{OH})_2$ to simulate the recycle of spent $\text{Ca}(\text{OH})_2$. Samples of Clinch River fly ash, $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ at weight ratios of 3/1/0, 3/1/0.5, and 3/1/1 were slurried at 90 °C with no NaOH added to the slurry. The collected solids were dried and tested for reactivity towards SO_2 and for conversion of the silicon of the fly ash. The results are presented in Figure 9.

Figure 9 shows that CaSO_3 has a beneficial effect on the solids reactivity towards SO_2 for long slurry times, but for short slurry times there is no noticeable effect. The beneficial effect at long slurry times increases with the amount of CaSO_3 present in the slurry. The data from the selective dissolution experiments shows that the presence of CaSO_3 has no effect on the conversion of silicon of the fly ash (not shown). This is expected since the presence of CaSO_3 does not affect the pH of the slurry and therefore does not affect the fly ash dissolution rate. The beneficial effect of the CaSO_3 must be due to a chemical reaction of the silicon or aluminum from the fly ash to produce solids which are reactive towards SO_2 . The reactive solids produced when CaSO_3 is present in the slurry are probably the ettringite-like materials that were observed by Jozewicz and Rochelle (2). It seems that the effect of CaSO_3 is only important for longer slurry times, that is, when the conversion of the fly ash is high and there is silicon or aluminum present to react with the CaSO_3 to form the ettringite-like materials.

The data from the fly ash dissolution experiments indicate that the silica and alumina present in the high calcium fly ash is much more reactive than the silica and aluminum present in the low calcium fly ash. This indicates that the presence of CaSO_3 in the high calcium fly ash slurry would have a strong effect on the product solids reactivity towards SO_2 , due to the high production of reactive, calcium-alumino-sulfite materials. Future experimental work will investigate this theory.

Comparing fly ash dissolution with reaction of fly ash with $\text{Ca}(\text{OH})_2$

The results from the fly ash dissolution experiments can be compared with the data obtained from the use of the selective dissolution method on the solids produced by the reaction of fly ash with $\text{Ca}(\text{OH})_2$. A major difference between the fly ash dissolution and the fly ash with $\text{Ca}(\text{OH})_2$ reaction experiments is the presence of the calcium silicate surface layer on the fly ash particle for the latter experiments. Figure 8 shows that this layer negatively affects the rate of silica dissolution from the fly ash. The data from Figure 5 show that the activation energy for the fly ash/ $\text{Ca}(\text{OH})_2$ reaction is only 6.8 kcal/mol versus 19.3 kcal/mol for the fly ash dissolution experiments. This indicates that the diffusion of the hydroxide ion becomes an important step when the product layer is present and suggest that this diffusion may, in some cases, actually control the overall rate of the reaction between fly ash and $\text{Ca}(\text{OH})_2$.

Relating Reactivity to Composition of Surface

It has been shown in experiments with $\text{Ca}(\text{OH})_2$ and diatomaceous earth, a reactive source of silica, that there is an optimum ratio of $\text{Ca}(\text{OH})_2$:diatomaceous earth for the production of solids for FGD (5). It has also been shown that the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids towards SO_2 is affected by the dissolved calcium concentration in the reacting slurry (6). Therefore, it is reasonable to assume that the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids depends on the ratio of calcium to silica in the surface layer of the solids.

The reactivity of the solids towards SO_2 , as determined by the sand bed reactor experiments, was correlated with the ratio of SiO_2 : CaO on the surface of these solids, as determined by the selective dissolution experiments. The correlation is shown in Figure 10 and the data are listed in Table 2.

The data show that the reactivity of the solids towards SO_2 is a linear function of the SiO_2 : CaO on the surface of the solids. The correlation is for all of the solids produced and tested, that is, it includes the effects of slurry temperature, $[\text{NaOH}]$, fly ash type, and fly ash: $\text{Ca}(\text{OH})_2$ ratio. However, it does not include the data from the solids produced when CaSO_3 was present in the slurry.

Also shown in Figure 10 is the data by Jozewicz et al., (5) for solids prepared by slurrying diatomaceous earth with $\text{Ca}(\text{OH})_2$. These solids were not actually tested with the selective dissolution method, rather, the ratios of SiO_2 : CaO of the solids were estimated to be the ratios of the materials added to the slurry. This assumption is probably valid due to the long slurry time (4 hr), the high slurry temperature (90°C), and the high reactivity of the diatomaceous earth. Figure 10 shows that the data of Jozewicz agree with the data obtained in this study.

CONCLUSIONS

The data from the sand bed reactor tests were correlated with the data from the selective dissolution experiments to show that the solids reactivity towards SO_2 depends linearly on the ratio of SiO_2 : CaO on the surface of the fly ash solids. The data agree with those of Jozewicz which showed that the most reactive solids produced by slurrying $\text{Ca}(\text{OH})_2$ with diatomaceous earth were those slurried at a ratio of 1:1 CaO : SiO_2 . The selective dissolution test is a very useful screening tool since it is much easier and faster to obtain data than performing experiments with the sand bed reactor. The correlation of solids reactivity towards SO_2 with the SiO_2 : CaO determined by the selective dissolution method is somewhat weak however, and future work will aim at increasing the accuracy of the selective dissolution method.

The fly ash dissolution experiments have shown that the dissolution rate of silica from the low calcium fly ash is approximately first order with respect to the NaOH concentration in the slurry. This would suggest that the reaction rate of this fly ash with $\text{Ca}(\text{OH})_2$ would also be first order with respect to the NaOH concentration in the slurry.

The dissolution rate of aluminum from the low calcium fly ash was also found to increase with NaOH concentration in the slurry, although the reaction order of aluminum dissolution with respect to hydroxide was only 0.83. The data showed that for low silicon conversions, the conversion of the aluminum in the fly ash was higher than the conversion of silicon in the fly ash, but for high silicon conversions, the conversion of the aluminum was lower than the conversion of the silicon.

The fly ash dissolution experiments also showed that the high calcium fly ashes are much more reactive than are the low calcium fly ashes. Based on these experiments, it is concluded that the high calcium fly ashes have a large amount of very reactive material that dissolves almost instantaneously. This material is richer in aluminum than in silica. The high availability of the silicon and aluminium of the high calcium fly ash indicates that the solids would rapidly react to form calcium silicate materials which are reactive towards SO_2 . Another advantage of the high calcium fly ashes is the presence of a large amount of calcium in the fly ash which can be utilized for reaction with SO_2 . In short, it appears

that high calcium fly ashes are more attractive for the production of reactive solids for use in FGD systems.

The sand bed reactor tests indicate that the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids towards SO_2 increases when CaSO_3 is present in the slurry. However, the data from the selective dissolution experiments show that the presence of CaSO_3 does not affect the conversion rate of silica from the fly ash. The later result is expected because the presence of CaSO_3 does not affect the hydroxide concentration in the slurry which controls the dissolution rate of the fly ash. The beneficial effect of the CaSO_3 is most probably due to a chemical interaction of the CaSO_3 with the silica or aluminum that dissolves from the fly ash. The products of this interaction are probably calcium-alumino-sulfite materials which evidently have a high reactivity towards SO_2 .

The production of these reactive, calcium-alumino-sulfite materials when CaSO_3 is present in the slurry would probably be greater for the high calcium fly ashes due to the high reactivity of the aluminum present in these fly ashes. However, this has not been demonstrated experimentally, so future work will investigate this hypothesis.

The comparison of the data from the fly ash dissolution experiments with the data from the selective dissolution experiments suggests that the presence of the calcium silicate surface layer on the surface of the fly ash- $\text{Ca}(\text{OH})_2$ solids inhibits the conversion of the silica from the fly ash. The activation energy for the conversion of the silica from the fly ash was found to be 19.3 kcal/mole for the fly ash dissolution experiments and only 6.8 kcal/mole. This inhibiting effect is subject to question, however, since it is not certain that the selective dissolution method is dissolving all of the material on the surface of the fly ash- $\text{Ca}(\text{OH})_2$ solids. Future work will clarify this question.

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TABLE 1. FLY ASH CHARACTERIZATION BY ASTM METHODS

Fly Ash	Composition as Oxides (%)			
	CaO	SiO ₂	Al ₂ O ₃	FeO
Clinch River*	4.0	57.0	27.0	8.0
Deseret	3.7	45.9	24.2	4.7
Fayette	26.3	33.3	24.1	5.8
Harrington	29.9	32.2	22.2	5.0
Laramie River*	30.0	35.0	17.0	6.0

* Analyzed with XES

TABLE 2. DATA FROM REACTIVITY AND SELECTIVE DISSOLUTION EXPERIMENTS

Slurry ¹ Composition	Fly Ash	Slurry Temp. (°C)	Slurry Time (hr)	Ca(OH) ₂ ² Conv. (%)	SiO ₂ :CaO ³ (mol/mol)
Ca(OH) ₂	-	-	-	18	0.000
3/1/0/0	Clinch R.	65	7	20	0.053
3/1/0/0	Clinch R.	65	8	21	0.051
3/1/0/0	Clinch R.	90	3	28	0.134
3/1/0/0	Clinch R.	90	5	53	0.304
3/1/0/0	Clinch R.	90	8	52	0.474
3/1/0/0	Clinch R.	155	1	59	-
3/1/0/0	Clinch R.	155	2	51	-
2.3/1/0/0	Clinch R.	160	2	46	0.328
3/1/0/0.18	Clinch R.	90	1	48	0.180
3/1/0/0.18	Clinch R.	90	3	62	0.380
3/1/0/0.18	Clinch R.	90	5	64	0.513
3/1/0/0.18	Clinch R.	90	8	62	0.645
3/1/0.5/0	Clinch R.	90	3	23	0.065 ⁴
3/1/0.5/0	Clinch R.	90	5	52	0.190 ⁴
3/1/0.5/0	Clinch R.	90	8	60	0.362 ⁴
3/1/1/0	Clinch R.	90	3	28	0.059 ⁴
3/1/1/0	Clinch R.	90	5	60	0.231 ⁴
3/1/1/0	Clinch R.	90	8	74	0.416 ⁴
5/1/0/0.30	Clinch R.	90	2	47	0.380
5/1/0/0.30	Clinch R.	90	4	56	0.610
5/1/0/0.30	Clinch R.	90	7	57	0.830
1/1/0/0	Si Fume	90	1	70	0.718
1/1/0/0	Si Fume	90	7	85	0.962
3/1/0/0	Fayette	90	3	49 ⁵	0.324
3/1/0/0	Fayette	90	5	69 ⁵	0.502
3/1/0/0	Fayette	90	9.33	62 ⁵	0.645
3/1/0/0 ⁶	Clinch R.	90	14	69	0.772
3/1/0/0 ⁶	Clinch R.	90	14	75	0.772

¹ 3/1/0.5/0.0 = 3g Fly Ash/1g Ca(OH)₂/0.5g CaSO₃•0.5 H₂O/0.0 M NaOH

² As determined in sand bed reactor tests

³ Determined by selective dissolution method

⁴ Estimated based on silica conversion observed and total Ca(OH)₂ added to slurry.

⁵ Corrected conversion for calcium from fly ash as determined by selective dissolution.

⁶ Sample prepared by Accurex Corporation.

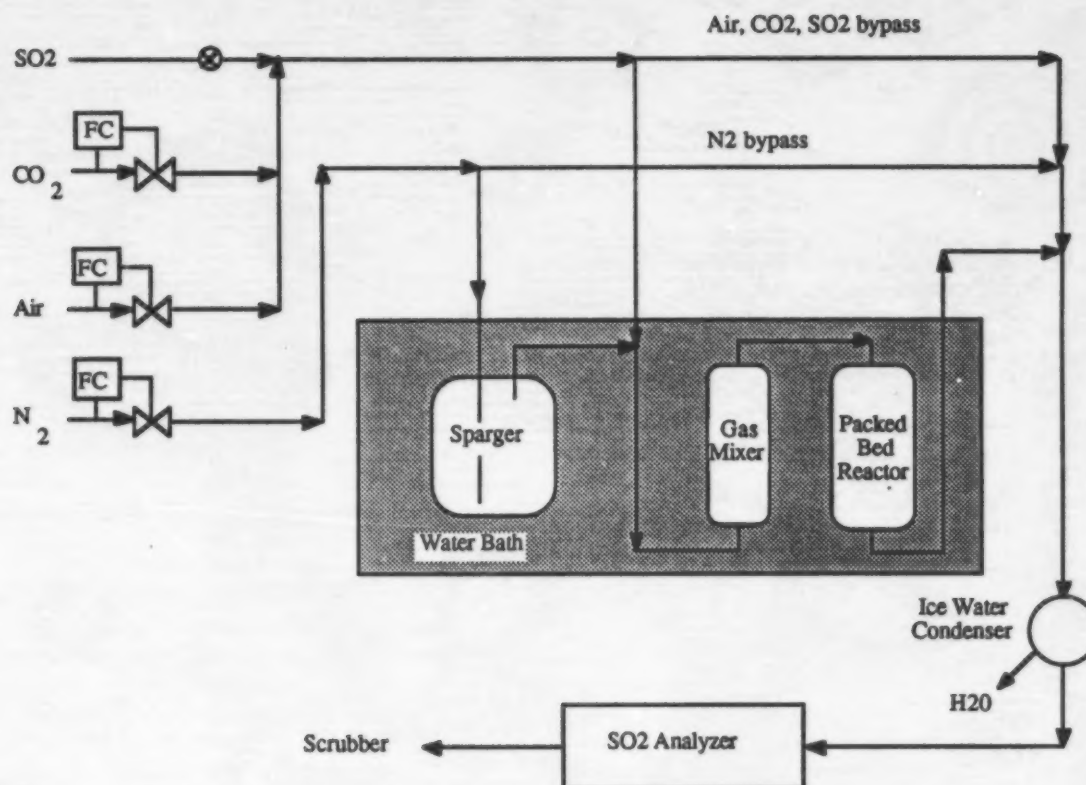


Figure 1. Packed Bed Reactor System

Reactor Conditions: 66 °C; 51 % R.H.; 4.6 l gas/min - 7% O₂, 10% CO₂, 83% N₂; 450 ppm SO₂; 1 hr reaction time.

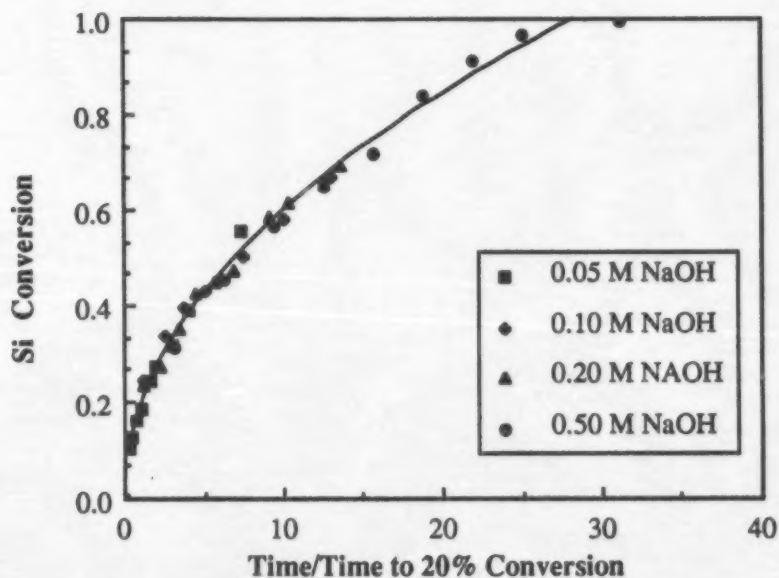


Figure 2. Effect of NaOH concentration on fly ash dissolution.

Dissolution conditions : 90 °C, 1.25 g Clinch River fly ash/liter; 5 g Na₂EDTA/liter; stir speed : 1000 rpm.

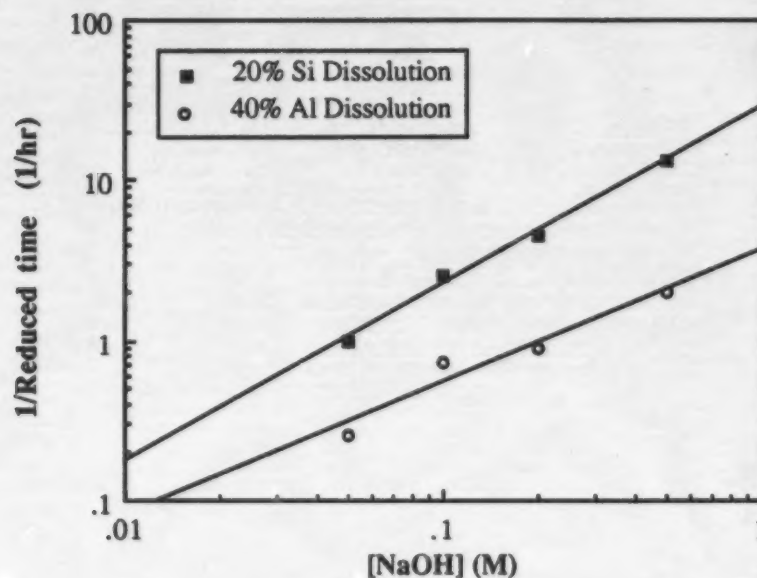


Figure 3. Determining the order of fly ash dissolution with respect to NaOH.
Dissolution conditions : 90 °C, 1.25 g Clinch River fly ash/liter; 5 g Na₂EDTA/liter;
stir speed : 1000 rpm.

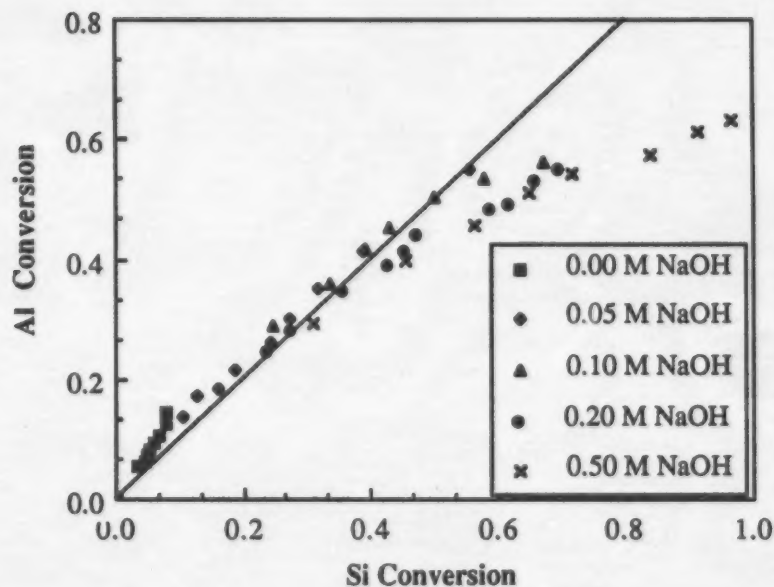


Figure 4. Comparing rates of silicon and aluminum dissolution.
Dissolution conditions : 90 °C, 1.25 g Clinch River fly ash/liter; 5 g Na₂EDTA/liter;
stir speed : 1000 rpm.

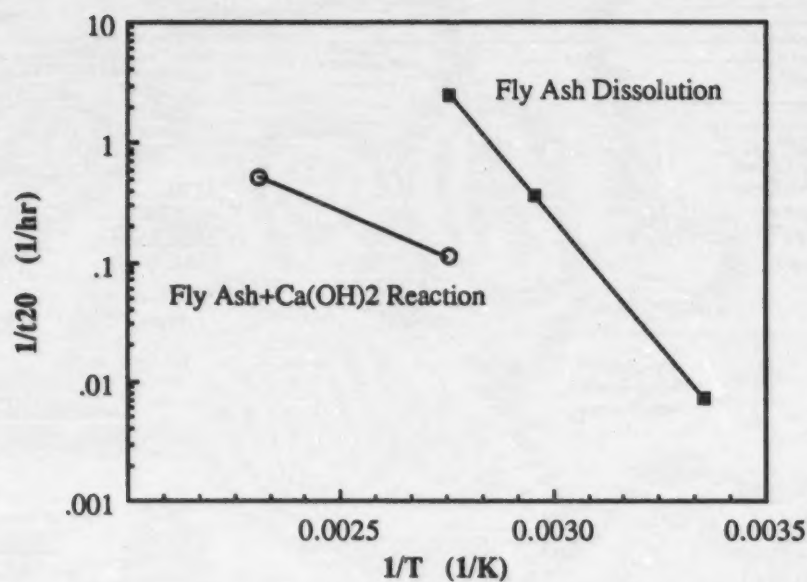


Figure 5. Arrhenius plots for fly ash dissolution and fly ash+Ca(OH)₂ reaction experiments. Clinch River fly ash

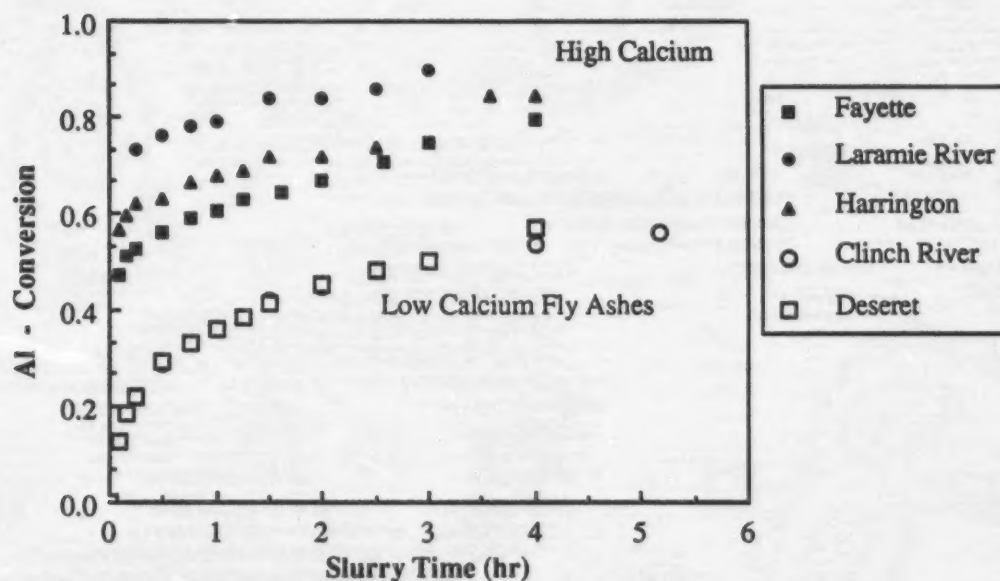


Figure 6. Effect of fly ash type on aluminum dissolution.
Dissolution conditions : 90 °C, 1.25 g fly ash/liter; 5 g Na₂EDTA/liter; 0.1 M NaOH, stir speed : 1000 rpm.

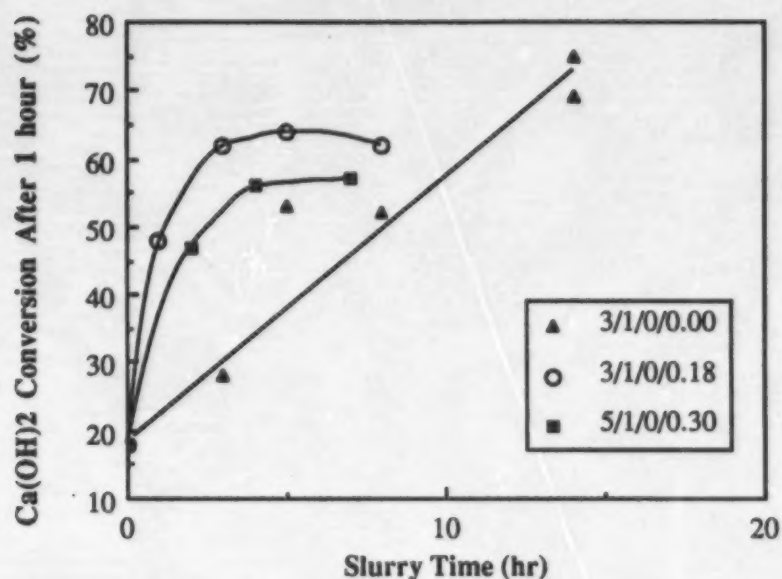


Figure 7. Effect of slurry conditions on the solids reactivity towards SO_2 .
 Reactor Conditions: 66 °C; 51 % R.H.; 4.6 l gas/min - 7% O_2 , 10% CO_2 , 83% N_2 ; 450 ppm SO_2 ; 1 hr reaction time.
 Slurry Conditions : 90 °C, 26% solids in slurry, Clinch River fly ash.
 3/1/0/0.18 = 3g fly ash/1g $\text{Ca}(\text{OH})_2$ /0 g CaSO_3 /0.18 M NaOH

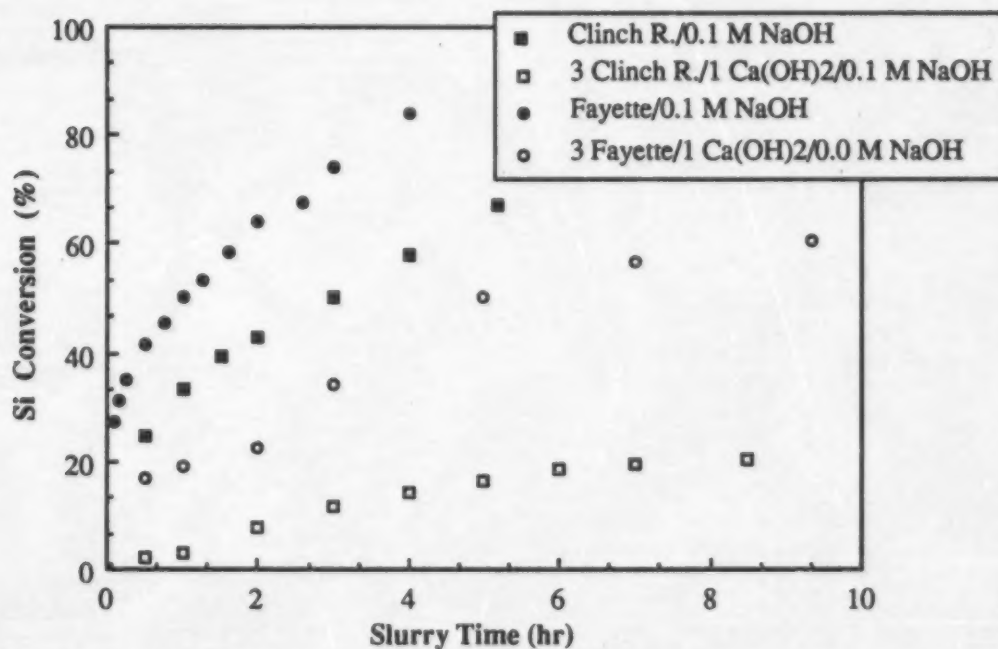


Figure 8. Effect of fly ash type on the conversion of fly ash.
 Dissolution conditions : 90 °C, 1.25 g fly ash/l, 5 g Na_2EDTA /l
 Reaction Conditions : 90 °C, 26% solids.

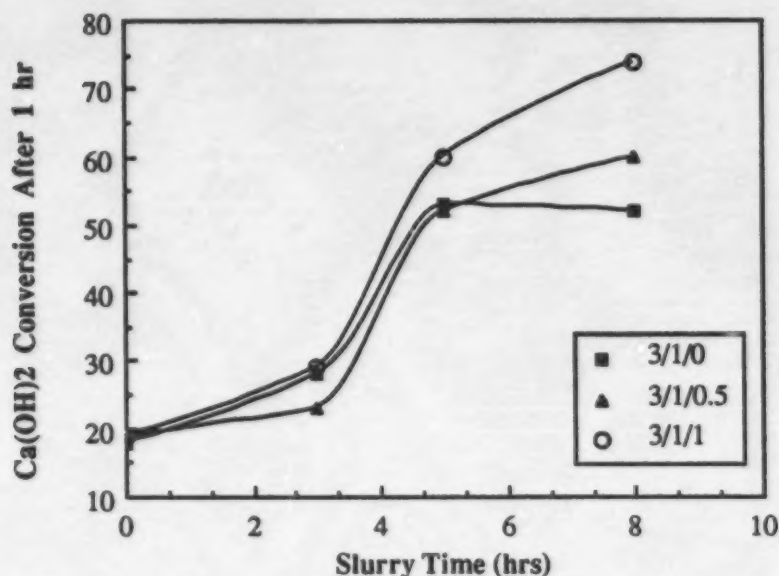


Figure 9. Effect of CaSO_3 on solids reactivity towards SO_2 .

Reactor Conditions: 66 °C; 51 % R.H.; 4.6 l gas/min - 7% O_2 , 10% CO_2 , 83% N_2 ; 450 ppm SO_2 ; 1 hr reaction time.

Slurry Conditions : 90 °C, 26-30% solids in slurry, Clinch River fly ash, no NaOH
 3/1/1 = 3g fly ash/1g Ca(OH)_2 /1 g $\text{CaSO}_3 \cdot 0.5 \text{H}_2\text{O}$.

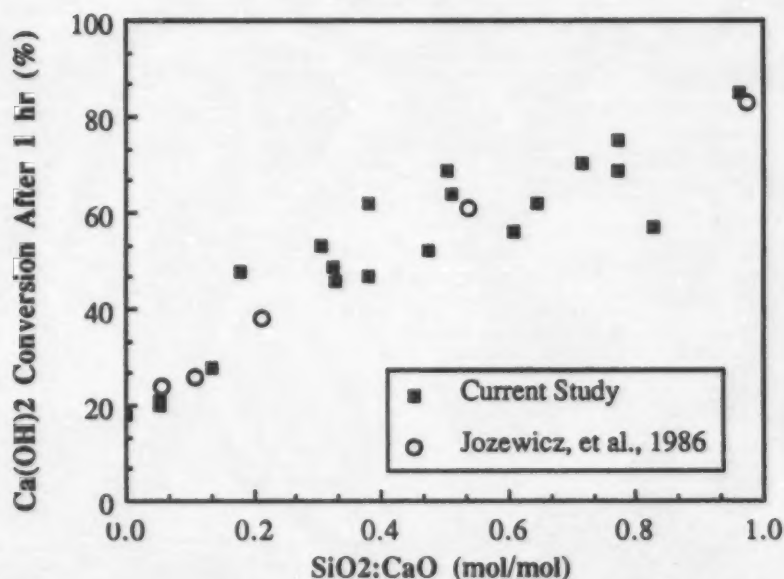


Figure 10. Effect of surface composition on solids reactivity.

Reactor Conditions: 66 °C; 51 % R.H.; 4.6 l gas/min - 7% O_2 , 10% CO_2 , 83% N_2 ; 450 ppm SO_2 ; 1 hr reaction time. (This study).

Reactor Conditions: 64.4 °C; 60 % R.H.; 4.6 l N_2 /min; 500 ppm SO_2 ; 1 hr reaction time. (Jozewicz, et al., 1986)

**PHYSICAL AND CHEMICAL ACTIVATION OF FLY ASH
TO PRODUCE REAGENT FOR DRY FGD PROCESSES**

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ABSTRACT

Previous workers have shown that fly ash can be reacted with lime to produce solids which are very reactive towards SO_2 at bag filter conditions. The present study shows that wet grinding of the fly ash prior to the reaction with lime dramatically increases the reactivity of the fly ash-lime solids. The solids prepared with the ground fly ash were two to three times as reactive as those prepared with the unground fly ash when tested in a bench scale duct injection system. The grinding of high calcium fly ash produced extremely reactive solids without the addition of lime due to the pozzolanic reaction between the calcium and the silicon of the high calcium fly ash in the wet grinder. The ground high calcium fly ash was slurried at an elevated temperature, and the subsequent bench scale duct injection tests showed a sharp increase in the removal efficiency of SO_2 when compared with unground high calcium fly ash. Slurries of the solids were also tested in a bench scale spray dry scrubber in which case the ground high calcium fly ash showed a removal of SO_2 similar to that of lime based slurry.

INTRODUCTION

Wet-dry scrubbing and duct-injection are two examples of low temperature techniques to control the SO_2 emissions from coal-fired industrial and utility boilers. The capital cost for the duct-injection systems is lower than that for the wet-dry scrubbing systems, but the removal efficiency is higher for the wet-dry systems. Therefore, a highly reactive sorbent must be used in duct injection systems to achieve acceptable SO_2 removal.

In wet-dry scrubbing, an alkaline slurry is sprayed into an drying vessel where the finely atomized slurry is contacted with the hot flue gas from the boiler. The sensible heat of the flue gas evaporates the

water from the droplets to give a dry product at the outlet of the spray dryer. Simultaneously, the SO_2 present in the flue gas dissolves into the water droplets and reacts with the alkaline sorbent (usually slaked lime). The dry reacted product is then collected in a particulate collector, usually a baghouse or an ESP, where additional reaction of the SO_2 with the dry particles can occur. A baghouse is the preferred method of collection, since the degree of gas/solid contact is higher in a baghouse than in an ESP. This increased gas/solid contact gives rise to a greater reaction between the SO_2 and the dry particles.

In a duct-injection system, a dry powdered sorbent is introduced into the humidified flue duct ahead of the particulate collector. Therefore, the SO_2 reacts with the solid sorbent only under dry conditions. Since the SO_2 removal occurs in both the duct and the particulate collector, the baghouse is again the preferred particulate control device.

Previous workers have shown that highly alkaline fly ash can be used to remove SO_2 in wet-dry scrubbing [1], [2], [3]. However, Petersen and Karlsson [3] have shown that a mixture of highly alkaline fly ash and slaked lime produced no improvement in SO_2 removal in the spray dryer when compared with slaked lime alone.

Recently, work has been performed to produce highly reactive sorbents using fly ash from coal-fired boilers [4], [5], [6]. In bench scale experiments using a packed bed reactor, Jozewicz and Rochelle [4] have shown that the slurring of fly ash with $\text{Ca}(\text{OH})_2$ produced solids which were much more reactive than slaked lime at bag filter conditions. In pilot plant experiments, Jozewicz et al. [5], showed that these fly ash based solids were much more reactive than slaked lime and that the solids were able to remove about 85 % of the SO_2 present in the flue gas using an approach to saturation temperature of 11 °C. However, to achieve these results, the fly ash and $\text{Ca}(\text{OH})_2$ had to be slurried for 12 to 16 hours at 90 °C, and the stoichiometric ratio of the alkaline sorbent had to be 1.8.

The purpose of this investigation was to study the effect of fly ash grinding on the reactivity of the solids produced by slurring the ground fly ash with $\text{Ca}(\text{OH})_2$. Wet grinding has previously been investigated for the purpose of producing reactive limestone for wet-dry scrubbing [7] and for the purpose of reactivating recycle material in lime based wet-dry scrubbing [8]. Two sources of ground and unground fly ashes were slurried with $\text{Ca}(\text{OH})_2$ and the product slurries were tested in a bench scale spray drying/duct injection system for reactivity towards SO_2 . The BET surface areas, the particle size distributions, and the water absorption isotherms were determined for the product solids. These solids were also examined using scanning electron microscopy.

EXPERIMENTAL APPARATUS AND PROCEDURE

SORBENT PREPARATION

The sorbents used in this study were produced using either a German, high calcium fly ash (HCFA) or by using an American, low calcium fly ash (LCFA). The sources and chemical compositions of these fly ashes are given in Table 1. The ashes were slurried at 85 °C in a one liter covered pyrex vessel for up to 24 hours. The fly ash loading was constant at 235 g fly ash / liter H_2O and the $\text{Ca}(\text{OH})_2$ loading was either zero or 75 grams $\text{Ca}(\text{OH})_2$ / liter H_2O . Slurry samples were normally taken every hour for six hours. These samples were cooled to room temperature and tested for reactivity towards SO_2 in a bench scale spray dryer/duct injection system.

The excess of the slurries used in the spray dryer/duct injection experiments were vacuum filtered and then dried in an atmospheric oven at 150 °C for two hours. The resulting solid samples were analyzed with scanning electron microscopy (SEM) using an ISI-100A instrument operating at 25 kV. The particle size of the samples was determined by re-slurrying them in 0.1% Dispex and analyzing the slurry with a Micromeritics Sedigraph 5000 D particle size analyzer. The solid surface areas were determined using N_2 as the adsorbate at 73 °K. The water absorption isotherms were also determined for these solids using a water absorption apparatus.

The two samples of fly ash were wet ground in a Netzsch® agitated ball mill (Type LME 4) before being slurried with the $\text{Ca}(\text{OH})_2$ to determine the effect of grinding on the reactivity of the fly ashes.

Eight kilograms of the fly ash were mixed with eight kilograms of water to give a total volume of approximately 11.5 liters. This mixture was circulated through the grinder. The total volume of the grinder was 4 liters, but 80 % of this volume was occupied by the Al_2O_3 balls (1.6 mm diameter). Therefore, the volume occupied by the fly ash-water mixture was only 0.8 liters.

The HCFA was ground for total of 1.25 hours and the LCFA was ground for a total of 4 hours. Therefore, the residence times of the fly ash particles in the grinder were only 5.2 and 16.7 minutes, respectively. The surface areas and the particle size distributions for the ground and unground fly ashes are given in Table 2.

APPARATUS

Wet-Dry Scrubber

The solids produced by the reaction of fly ash with $\text{Ca}(\text{OH})_2$ have potential use in low temperature (less than 150 °C) flue gas desulfurization systems. For this reason, the slurries of the fly ash based solids were tested for reactivity in a small bench scale spray drying apparatus.

The bench-scale spray dryer-baghouse system is shown in Figure 1. The apparatus dimensions and operating conditions are listed in Table 3. Synthetic flue gas was obtained by mixing SO_2 and CO_2 with house air. The gas flowrates were monitored with calibrated rotameters which operated at higher pressure (3 bar abs.) in order to obtain stable gas flow.

The total gas flow rate was 1500 NI/h (dry). In order to obtain the desired humidity at the inlet of the spray scrubber, the house air was sparged through tempered water. The degree of gas-liquid contact in the humidifier was sufficient for the gas to closely approach saturation. The humidified gas was then mixed with the water soluble gases (CO_2 and SO_2). The resulting gas was then passed through a packed, heated column to ensure that the gas was well mixed and heated to the desired spray dryer inlet temperature (150 °C).

The flue gas passed through an annular sieve plate at the top of the spray dryer. The function of the plate was to build up a pressure drop so that the gas distribution over the plate became even. The plug-flow residence time in the spray dryer was approximately 11 seconds (based on NTP).

The spray dryer and the baghouse vessels were constructed of glass with Teflon® tops. Both vessels were water jacketed to ensure that the humidity in the gas does not condense on the vessel walls. The temperature of the water jacket was the same as that of the spray dryer outlet gas (74 °C).

The slurry feed was introduced to the spray dryer through an ultrasonic nozzle manufactured by Sonotek® Corporation. Atomization was carried out by a piezoelectric crystal operating at a frequency of 60 kHz. The slurry left the atomizer at a very low speed and the average sauter diameter was approximately 25 μm . The feed pump was a peristaltic pump manufactured by LKB® which gave no noticeable pulsating of the slurry flow.

The flue gas entered the baghouse through a connection pipe from the spray dryer. The baghouse consisted of five filterbags of jet pulse-type. Using on-off valves, any combination of the five filterbags was possible. This made it possible to alter the air to cloth ratio from 0.007 m/s to 0.034 m/s (NTP). A reverse jet pulse of compressed air cleaned the filterbags and the dry product was collected in a sample bottle under the baghouse.

The sample gas could be taken from three different places: ahead of the spray dryer, between the spray dryer and the baghouse, or after the baghouse. A Binos® UV analyzer was used to determine the SO_2 concentration.

The experimental conditions for the bench-scale spray drying system were chosen to simulate actual conditions in larger spray drying systems. The inlet flue gas composition was 13.4% CO_2 , 11 % H_2O , 1000 ppm SO_2 , and the balance compressed air.

Each experimental run was started by spraying only distilled water into the spray chamber (i.e. no alkali was spray dried). The SO_2 concentration at the inlet was adjusted to 1000 ppm and the system was allowed to reach steady state (when the SO_2 concentration after the baghouse reached approximately 1000 ppm). The feed pump was then switched to the slurry and the flowrate was increased. The increase in the flowrate was necessary to keep a constant spray dryer outlet temperature (74°C).

The SO_2 concentration after the spray dryer adjusted quickly to a steady state value after the alkali was fed to the spray dryer. The SO_2 concentration leaving the baghouse did not change as rapidly, however. The concentration continued to change as a filter cake was built up on the fabric filter. The SO_2 removal across the spray dryer was the difference between the inlet and outlet SO_2 concentrations of the spray dryer, and the removal across the baghouse was the difference between the SO_2 concentration at the outlet of the spray dryer and the SO_2 concentration at the outlet of the baghouse.

Duct Injection System

In order to test the fly ash based solids at duct injection conditions, it was only necessary to make minor changes in the spray dryer - baghouse apparatus. Actually, only two lines were changed: the sample line just before the baghouse was disconnected, and the acid-gas line from the rotameters was connected in its place. The compressed air still entered at the top of the spray dryer. The slurry was also injected at the top of the spray dryer and atomized using the Sonotek® nozzle. Thus, the slurry was still spray-dried, but not in the presence of the acid gas. The dried particles and air were then contacted with the SO_2 laden gas that was introduced in the ductwork between the spray dryer and the baghouse. This configuration allowed the particles to be easily dispersed into the flue gas.

In order to obtain the correct spray dryer outlet temperature (74°C), the inlet air temperature was raised from 150 to 210°C . This was necessary due to the decreased dry gas flow in the spray dryer under the duct injection configuration. The acid gas inlet stream was also heated to 74°C in order to give a flue gas temperature of 74°C . This corresponds to an approach to saturation temperature of 19°C .

It was decided to keep the filters free of a filter cake and report the SO_2 removal as that occurring in the ductwork. This was accomplished by thoroughly cleaning the filters before the run and also cleaning the filters during the run. The absence of the filter cake was apparent from the low pressure drop across the filters and by noticing that the mid-run filter cleanings did not change the SO_2 concentration of gas exiting from the baghouse.

Water Absorption Apparatus

The calcium silicate solids produced by slurrying fly ash with $\text{Ca}(\text{OH})_2$ have been shown to be much more reactive than $\text{Ca}(\text{OH})_2$ at bag filter conditions. These solids may be more hygroscopic than $\text{Ca}(\text{OH})_2$ and this may be a reason for the solids' increased reactivity towards SO_2 . To determine the solids' affinity for water, water absorption isotherms were determined using a water absorption apparatus for a wide variety of fly ash- $\text{Ca}(\text{OH})_2$ solids.

The water absorption apparatus is shown in Figure 2. The humidity chamber is comprised of three interconnected glass columns. The first column (3.2 cm diameter, 14 cm height) is surrounded by a furnace that is controlled at 250°C . Water is pumped into this packed column, evaporated and mixed with the carrier gas (house air) which also enters the top of the column. Thus, the first column serves to superheat steam and mix it with the dry air. The second (9.5 cm ID, 14.5 cm height) and third glass columns (9.5 cm ID, 24.5 cm height) are jacketed, and water at $\sim 70^\circ\text{C}$ is pumped through the jacket to bring the humidified gas to the correct temperature (70°C). The second column is also packed with small ($\sim 5\text{mm}$) pieces of 0.6 mm glass tubing to ensure that the gas- H_2O mixture is well mixed and at the desired temperature. The third column is hollow and contains a thermocouple and a weighing pan. The weighing pan stands on a weighing balance (Mettler # PM460) that is accurate to 0.001 grams. An infrared heating element is suspended above the sample pan to dry the sample before the start of the run. A heating lamp is used at the bottom of the third glass column to ensure that the humid gas coming out of the bottom of the column does not condense on the balance. An IBM compatible PC is interfaced with the water absorption apparatus. The PC controls the flowrate of the water pump and records the weight from the balance as well as the output from the thermocouple.

The carrier gas flows at 0.118 l/sec (424 Nl/h) and is monitored with a rotameter. Water is added to the system using a peristaltic pump (Ismatec #7618-32).

The water absorption isotherms for the fly ash- $\text{Ca}(\text{OH})_2$ solids were performed at 70°C. Approximately 5 grams of the dried sample were placed on the weighing pan, which was then inserted into the bottom glass cylinder of the humidification unit. The infrared heater was turned on to dry the sample (at 140 °C) and the equilibrium (dry) sample weight was recorded. After the heater was turned off, the samples gained weight - presumably due to the non-zero humidity of the gas passing through the chamber.

The relative humidity in the chamber was step changed every thirty minutes by changing the voltage signal that was sent from the PC to the pump. The PC recorded the sample weights every 20 seconds. A program written in Turbo Pascal® was used to determine the sample weights just before the flowrate change of the pump and to calculate the water absorption surface areas for the solids.

EXPERIMENTAL RESULTS

EFFECT OF GRINDING/COOKING ON SORBENT PROPERTIES

The excess of the slurries that were tested in the bench scale spray drying apparatus were vacuum filtered and then dried in an atmospheric oven at 150 °C for 2 hours. The resulting solids were then analyzed to determine the effect of grinding and high temperature slurrying on the solid properties. These solid samples were tested for BET nitrogen surface area and for particle size distribution. The solids were also analyzed with scanning electron microscopy (SEM). The water absorption isotherms were determined using the water absorption apparatus.

Low Calcium Fly Ash

Figure 3 shows the results from the BET analysis for the solids produced using the low calcium fly ash (LCFA). The data show that the solid surface areas increase with slurry time. The data also show that the surface areas for the solids prepared with the ground LCFA are much higher than those for the solids prepared with the unground LCFA.

The surface areas of the fly ash solids increase due to the production of calcium silicate solids on the surface of the fly ash [4]. The surface areas for the solids prepared with the ground LCFA are higher due to the increased production of calcium silicate solids when using ground fly ash. This is consistent with the work done by Jozewicz et al [5], who hypothesized that the rate limiting step of the reaction of fly ash with $\text{Ca}(\text{OH})_2$ was the dissolution of silica from the fly ash. The grinding of the LCFA increases the dissolution of the silica from the fly ash by reducing the particle size of the fly ash, and therefore increasing the surface area available for silica dissolution. The silica dissolution rate may also be favoured due to the exposure of the glass on the inside of the fly ash particles which may have a higher reactivity than the glass on the outer surface of the fly ash.

The production of high surface area solids is evident when comparing the SEM photographs of fly ash (Figure 4) with the photographs of the reacted solids (Figures 5 and 6). The unslurried fly ash particles are smooth, glassy particles with a low specific surface area (1 to 4 m²/g). The photograph of the unground LCFA slurried with $\text{Ca}(\text{OH})_2$ for six hours (Figure 5) shows that the fly ash particles have been coated with a high surface area material that is presumably a calcium silicate hydrate. The photograph of the ground LCFA slurried with $\text{Ca}(\text{OH})_2$ for five hours (Figure 6) shows that very high surface area solids have been produced. This photograph also shows that these ground, reacted solids are agglomerated and that they have approximately the same agglomerate size as the particle size for those produced with the unground LCFA.

The particle size distributions of several solid samples are given in Table 4. The data show that the low and high calcium fly ashes have approximately the same mean particle size (12 and 18 µm), but that the high calcium fly ash has a slightly smaller particle size distribution. These results are consistent with

that reported in the literature [8]. The table also shows that the high temperature slurring of the unground LCFA with $\text{Ca}(\text{OH})_2$ does not significantly affect the particle size distribution. This is consistent with the data obtained from SEM which showed that the slurried solids were nearly the same size as the original fly ash particles.

The particle size distribution data for the ground LCFA shows that the particle size is much smaller for the ground fly ash than for the unground fly ash. The data for the solids produced by slurring the ground LCFA with $\text{Ca}(\text{OH})_2$ shows that the mean particle size increases with slurring, but that it is lower than that for the solids produced using the unground LCFA. This increase in particle size may be due to the reaction of $\text{Ca}(\text{OH})_2$ with the silica from the fly ash, but the increase probably stems from the addition of large lime particles. The reaction produces very high surface area solids which then agglomerate easily. The discrepancy between the particle size using SEM and the particle size determined from the particle size analyser may result from the reslurring of the solids in Dispex. The ultrasonic bath that was used to facilitate the reslurring process may have broken up the agglomerates before the solids were analyzed in the particle size analyzer.

This agglomeration of the reacted solids is favorable, in one sense, because the larger particles will be easier to remove from the gas stream and there will be no very small particles emitted to the atmosphere. The emissions of very small particles is seen as a threat to the human respiratory system which allows the very small particles to be inhaled deeply into the lungs.

High Calcium Fly Ash

During the grinding of the high calcium fly ash (HCFA), a significant heat effect was observed, and the outlet slurry began to lose water due to evaporation from the hold tank. Therefore, more water was added to the hold tank (approximately 3 liters). The final solids content of the ground HCFA mixture was 35 %. The addition of water was not necessary during the grinding of the LCFA and no heat effect was observed. The final solids content of this mixture was determined to be 46 %.

The heat effect observed with the HCFA is believed to result from the slaking of the CaO present in the HCFA. By comparing the surface areas of the ground fly ashes (Table 2), it is clear that a reaction has taken place during the grinding of the HCFA. The surface area of the ground HCFA was nearly three times that of the ground LCFA (30.4 vs $13.3 \text{ m}^2/\text{g}$, respectively) even though the ground LCFA had a mean particle size that was 4 times smaller than ground HCFA.

Figure 7 shows the effect of high temperature slurring on the surface areas of the HCFA solids. It should be noted that these solids were slurried without $\text{Ca}(\text{OH})_2$, that is, the slurries consisted just of high calcium fly ash and water. The data show that the surface areas increase with high temperature slurring - presumably due to the production of high surface area calcium silicate materials. The data also show that the ground HCFA solids have a much higher surface area than do the unground HCFA solids.

Figure 7 also shows that the surface area of the ground HCFA increases from $30.4 \text{ m}^2/\text{g}$ to $40 \text{ m}^2/\text{g}$ after slurring for 1 hour, but that at longer slurry times the surface area is unchanged. This suggests that the reaction to produce calcium silicates is completed after 1 hour for the ground HCFA. This probably results from the depletion of the silica in the high calcium fly ash. The ratio of SiO_2 to CaO in the high calcium fly ash is only about 3:4. This compares with a ratio of about 2:1 for the LCFA + $\text{Ca}(\text{OH})_2$ case (Figure 3).

Therefore, a high calcium, high silicon fly ash might be the optimum fly ash to produce reagent for dry FGD processes.

Water Absorption Isotherms

The calcium silicate solids produced by slurring fly ash with $\text{Ca}(\text{OH})_2$ have been shown to be much more reactive than $\text{Ca}(\text{OH})_2$ at bag filter conditions. These solids may be more hygroscopic than $\text{Ca}(\text{OH})_2$ and this may be a reason for the solids' increased reactivity towards SO_2 . To determine the

solids' affinity for water, water absorption isotherms were determined using the water absorption apparatus for a wide variety of fly ash- $\text{Ca}(\text{OH})_2$ solids.

Figure 8 shows the results from the water absorption experiments for the solids prepared with the low calcium fly ash. The data show that the solids prepared by slurring unground LCFA (Un) with $\text{Ca}(\text{OH})_2$ (weight ratio 3:1) at 5 hours absorb more water than does $\text{Ca}(\text{OH})_2$, and that the unslurred LCFA does not absorb much water at all. Figure 8 also shows that the solids prepared with the ground LCFA absorb much more water than do the solids prepared with the unground fly ash.

Figure 9 shows the water absorption isotherms for the solids prepared from the high calcium fly ash. The data show that the unground HCFA has a low affinity for water, but that the affinity for water can be increased by high temperature slurring. The data also show that the ground HCFA absorbs much more water than do the solids prepared with the unground fly ash.

The water absorption data support the hypothesis that the fly ash - $\text{Ca}(\text{OH})_2$ solids are more reactive than $\text{Ca}(\text{OH})_2$ at bagfilter conditions because they have a greater affinity for water vapor. The data also suggest that the solids prepared with the ground fly ashes should be much more reactive than the solids prepared with the unground fly ashes when tested at bag filter conditions.

DUCT INJECTION

In order to determine the reactivity of the fly ash- $\text{Ca}(\text{OH})_2$ solids under duct injection conditions, the spray dryer - baghouse apparatus was reconfigured to run duct injection experiments (see the Apparatus section). The spray dryer was used to dry the "reacted" slurries in hot air and the dried particles and hot air were then contacted with an SO_2 laden gas stream. The filters were cleaned both before and during the runs to keep the filter cake to a minimum. Therefore, the SO_2 removal that is presented here is the removal in the ductwork, and the removal across the bagfilter is minimal.

Baseline Tests Using $\text{Ca}(\text{OH})_2$

To establish a baseline for the reactivity of the fly ash solids under duct injection tests, several experiments were performed using $\text{Ca}(\text{OH})_2$ as the sorbent. The $\text{Ca}(\text{OH})_2$ was a Swedish Limhamn type with a surface area of $14.6 \text{ m}^2/\text{g}$. These tests looked at the effect of $\text{Ca}(\text{OH})_2$ stoichiometric ratio on the removal of SO_2 under duct injection conditions. The inlet SO_2 concentration was 1000 ppm, and the approach to saturation temperature was 19°C . The results are presented in Figure 10.

The data show that the SO_2 removal increases from 19 % for a stoichiometric ratio of 1.0 to 39 % for a stoichiometric ratio of 3.0. This indicates that pure $\text{Ca}(\text{OH})_2$ would be a poor reagent choice for duct injection systems used for flue gas desulfurization. This was also concluded by Jozewicz et al.[5], who found that $\text{Ca}(\text{OH})_2$ gave very poor performance in pilot plant duct injection tests when compared to the solids produced by slurring $\text{Ca}(\text{OH})_2$ with fly ash.

Low Calcium Fly Ash

A series of experiments was performed to determine the effect of fly ash grinding on the reactivity of the solids produced by slurring the low calcium fly ash with $\text{Ca}(\text{OH})_2$.

The fly ash loading was 3 grams fly ash/g $\text{Ca}(\text{OH})_2$ and the slurry temperature was 85°C . NaOH was tested as an additive to the fly ash slurries, the NaOH concentration being either 0.0 or 0.1 M. The stoichiometric ratio of $\text{Ca}(\text{OH})_2$ to the SO_2 in the flue gas was constant at 1.0 and the approach to saturation temperature in the flue gas stream was 19°C . The data from these experiments are presented in Figure 11.

The data show that the reactivity of the unground LCFA + $\text{Ca}(\text{OH})_2$ solids increases from 17% SO_2 removal for a slurry time of '0' hours to 23.5 % removal for a slurry time of 5 hours. However, the SO_2 removal decreased to 18 % for a slurry time of 24 hours. When 0.1 M NaOH was added to the slurry, the reactivity of the unground LCFA + $\text{Ca}(\text{OH})_2$ solids increased to 23 % SO_2 removal for a 1 hour slurry time, but the reactivity steadily decreased to 14 % removal for a 24 hour slurry time. The

increase in reactivity at short slurry times probably results from the added alkalinity of the 0.1 M NaOH in the slurry. The decrease in reactivity when NaOH is present in the slurry for long slurry times has been reported before [10], and probably results from the production of unreactive calcium silicate solids.

The data show a large beneficial effect of wet grinding the fly ash before reacting it with $\text{Ca}(\text{OH})_2$. The SO_2 removal increased from 17 % at '0' hours slurry time to 35 % for the sample that was slurried for 3 hours. This increase in removal probably results from the production of high surface area, calcium silicate solids. The duct injection tests for the ground LCFA solids were impossible for slurry times longer than 3 hours due to the increased viscosity of the fly ash - $\text{Ca}(\text{OH})_2$ slurry. The peristaltic slurry pump which was connected to the atomizing nozzle of the spray dryer could not pump the thick slurry for the 5 hour test. The reason for the increased viscosity is the production of the high surface area solids.

Although the SO_2 removal of the ground fly ash solids approaches only 40 % in this system, it should be noted that the removal in the baghouse would be great if a filter cake was present. In a pilot plant duct injection system using unground fly ash + $\text{Ca}(\text{OH})_2$ solids, Jozewicz et al. [5], reported that only 1/3 of the SO_2 removal occurred in the ductwork and 2/3 occurred in the baghouse. For a stoichiometric ratio of 1.8, Jozewicz et al. [5], reported a total removal of approximately 80 % for the unground fly ash + $\text{Ca}(\text{OH})_2$ solids that were slurried for 12 hours. Since the ground fly ash solids presented here are much more reactive in the ductwork than are the unground solids, it is assumed that the overall performance (duct + baghouse) of the ground solids would be much greater than the unground solids.

High Calcium Fly Ash

Previous workers have shown that high calcium fly ash (HCFA) could be activated for reactivity towards SO_2 by high temperature slurring. In experiments using a bench scale reactor designed to simulate bagfilter conditions, Peterson and Rochelle [10] showed that the reactivity of the HCFA could be increased to a level comparable to that of the LCFA + $\text{Ca}(\text{OH})_2$ solids. In order to examine the reactivity of the high calcium fly ash solids under duct injection conditions, several attempts were made to produce reactive solids from HCFA alone (i.e. without $\text{Ca}(\text{OH})_2$).

The HCFA was slurried at a loading of 210 g fly ash/liter H_2O and at 85 °C. NaOH was tested as an additive to the slurry, its concentration being either 0.0 or 0.1 M. The stoichiometric ratio was one, based on the calcium in the HCFA. The inlet SO_2 was 1000 ppm and the approach to the saturation temperature was 19 °C. The results from these experiments are presented in Figure 12.

The data show that high temperature slurring of the unground HCFA did not change the reactivity of the HCFA under duct injection conditions. The ash removed 11 % of the SO_2 whether it was slurried for '0' hours or for 4 hours. The addition of 0.1 M NaOH to the unground HCFA slurry produced only a small increase in the SO_2 removal.

The effect of wet grinding the HCFA was great. The ground ash slurried for '0' hours removed 32 % of the SO_2 and a slurry time of 1 hour increased this removal to 40 %. Longer slurry times produced no further improvement.

The reactivity of the ground HCFA solids can be related to the surface area data (Figure 7). The surface area increases from 30.4 m^2/g for the unslurried ash to 40 m^2/g for the ash slurried for 1 hour, but longer slurry times showed no improvement in the solid surface area. The reactivity data and the surface area data give weight to the hypothesis that the reactivity of the ground HCFA solids is limited by the low amount of silica in the HCFA. This indicates that a very reactive sorbent could be obtained by wet grinding a high calcium, high silicon fly ash.

SPRAY DRYING

It has been reported that the fly ash- $\text{Ca}(\text{OH})_2$ slurries cannot be spray dried at normal approach to saturation temperatures in the spray dryer. In pilot plant experiments, Jozewicz et al. [5], showed that the slurries produced by slurrying fly ash with $\text{Ca}(\text{OH})_2$ for 12 hours at 90 °C could not be spray dried

unless the approach to saturation temperature was at least 75 °C. At these high approach temperatures, however, the reactivity towards SO₂ becomes very low because the relative humidity in the flue gas is very low. However, in the present study no problems were seen when spray drying the sorbents investigated. The present study examined the effects of slurring time and grinding on the reactivity of the fly ash based slurries in the spray dry scrubber.

Low Calcium Fly Ash

Several experiments were performed to determine the effect of slurry time on the reactivity of the fly ash-Ca(OH)₂ slurries. The LCFA was slurried with Ca(OH)₂ at a weight ratio of 3:1 for up to 5 hours at 85 °C. The total solids loading in the slurries was 280 g/liter H₂O. The flue gas inlet to the spray dryer contained 1000 ppm SO₂ and the approach to saturation temperature at the outlet of the spray scrubber was near 19 °C. The stoichiometric ratio of Ca(OH)₂ to SO₂ was constant at 0.82 for all of the experiments. The results are presented in Figure 13.

The data show that the LCFA has a very small effect on SO₂ removal in the spray dryer. The steady decrease with slurring time for the slurries of the unground LCFA and Ca(OH)₂ may be explained by alterations in the drying characteristics for these slurries. The removal decreased from 47.5 % to 36 % as the slurry time increased from 1 to 5 hours. It should be noted here that Ca(OH)₂ under the same experimental conditions removed 56 % of the SO₂ in the flue gas.

Figure 13 shows that the reactivity of the slurries produced using the ground LCFA does not decrease with slurry time. This can be explained by the much higher surface areas of the solids produced using the ground LCFA. The high surface areas of these solids leads to a higher reactivity in the spray dryer which offsets the lower reactivity due to the altered drying characteristics.

High Calcium Fly Ash

Several experiments were performed to evaluate the possibility of producing reactive slurries by the grinding of high calcium fly ash. The flue gas contained 1000 ppm SO₂ and the outlet temperature of the spray dryer was 74 °C. The results are presented in Figure 14.

The data show that the slurries of the ground HCFA were almost as reactive as the slurries of Ca(OH)₂ when judged on a calcium stoichiometric basis. The spray dryer nozzle could only atomize slurries of up to 30 wt % solids, however, so the removal of SO₂ was limited to 56 % for the ground HCFA slurries due to the high amount of inert material in the fly ash. However, the data show that the slurries of ground HCFA are much more reactive than the slurries of the unground HCFA.

Due to the low removal of SO₂ experienced using the ground HCFA solids alone, several experiments were performed using slurries that contained a combination of ground HCFA and Ca(OH)₂. The ground HCFA and the Ca(OH)₂ were slurried together at room temperature for 20 minutes before being tested in the spray drying apparatus. The amount of ground HCFA was constant at a stoichiometric ratio (SR) of 0.7 (based on the calcium content of the fly ash) and the Ca(OH)₂ was varied from SR=0.5 to SR=1.5. The results are presented in Figure 15.

The data show that the addition of the ground HCFA to the Ca(OH)₂ slurries dramatically improves the SO₂ removal in the spray dryer. This compares to no improvement for the addition of the unground HCFA to the Ca(OH)₂ slurries [3]. These data show that the ground HCFA has very good potential use as a substitute for part of the Ca(OH)₂ reagent used in wet-dry scrubbers.

CONCLUSIONS

The present study has shown that the wet grinding of fly ash is very beneficial for the production of highly reactive sorbents for use in low temperature flue gas desulfurization systems. The grinding increases the reactivity of the fly ash-based sorbents and greatly reduces the slurring time needed to produce the sorbents. The data presented also show that highly reactive sorbents can be produced by the wet grinding of high calcium fly ash due to the pozzolanic reaction between the calcium and the silica of the fly ash in the wet grinder. The data suggest that a very reactive sorbent could be produced by the grinding of a fly ash that has both a high calcium and a high silica content.

The data have shown that the sorbents produced using ground low calcium fly ash are much more reactive than those produced using the unground fly ash when the sorbents were tested under duct injection conditions. These data, along with the water absorption and BET surface area data, also suggest that the ground fly ash solids would be much more reactive than the unground fly ash solids when tested at bag filter conditions.

The current study has also shown that pure ground high calcium fly ash can be used in a spray dry scrubber. The ground high calcium fly ash reactivity towards SO_2 is almost the same as $\text{Ca}(\text{OH})_2$ based on the stoichiometry of calcium. The use of ground low calcium fly ash slurry did not lead to any improvement in the removal of SO_2 in the spray dryer compared with pure slaked lime while the use of unground lead to a small decrease of spray dryer performance.

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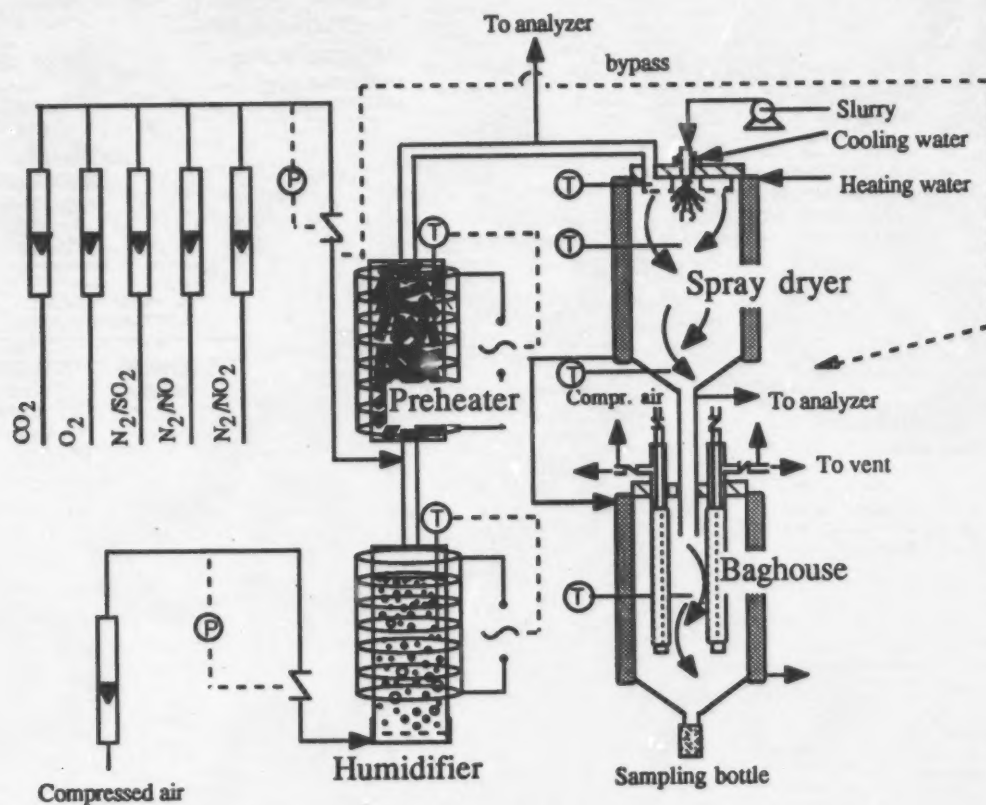


Figure 1. Spray drying/duct injection apparatus.

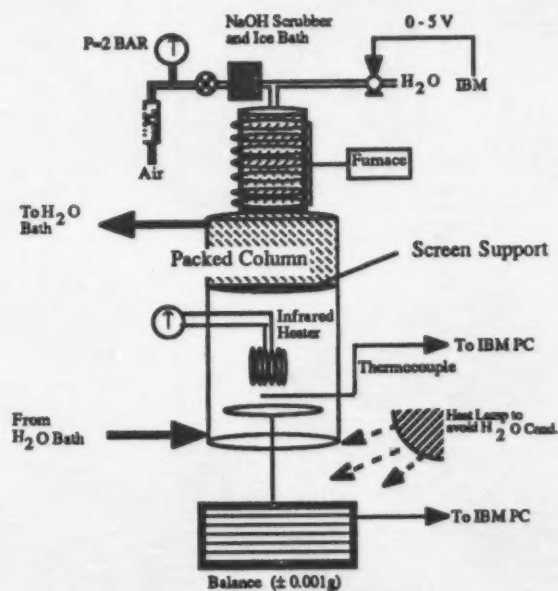


Figure 2. Water absorption apparatus.

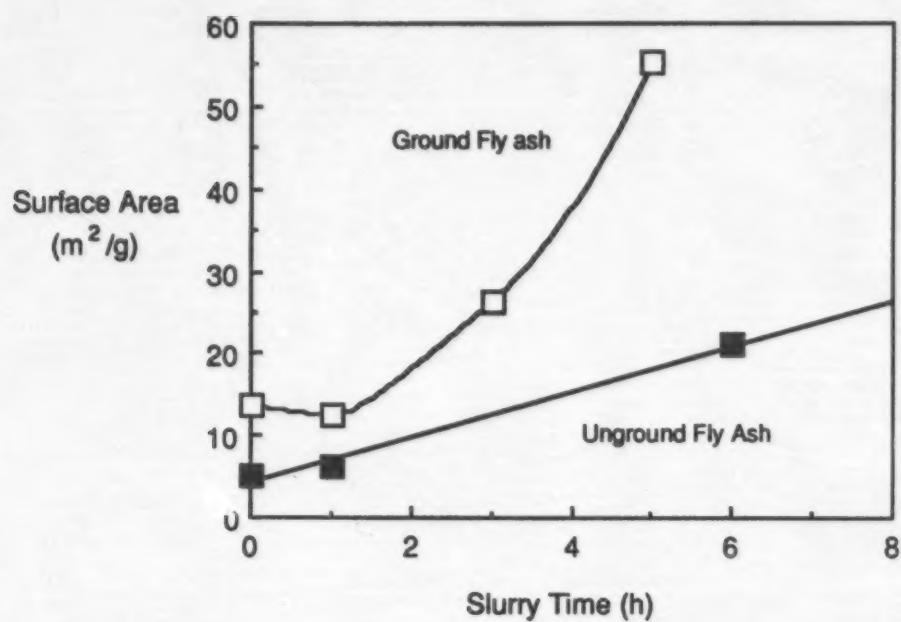


Figure 3. The Effect of fly ash grinding on the surface areas of the LCFA solids.

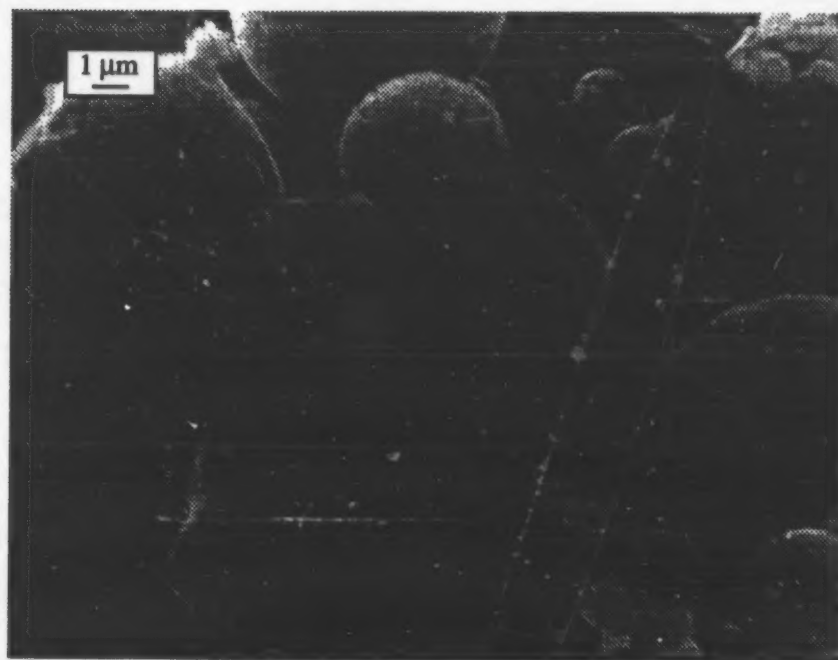


Figure 4. SEM photograph of LCFA.

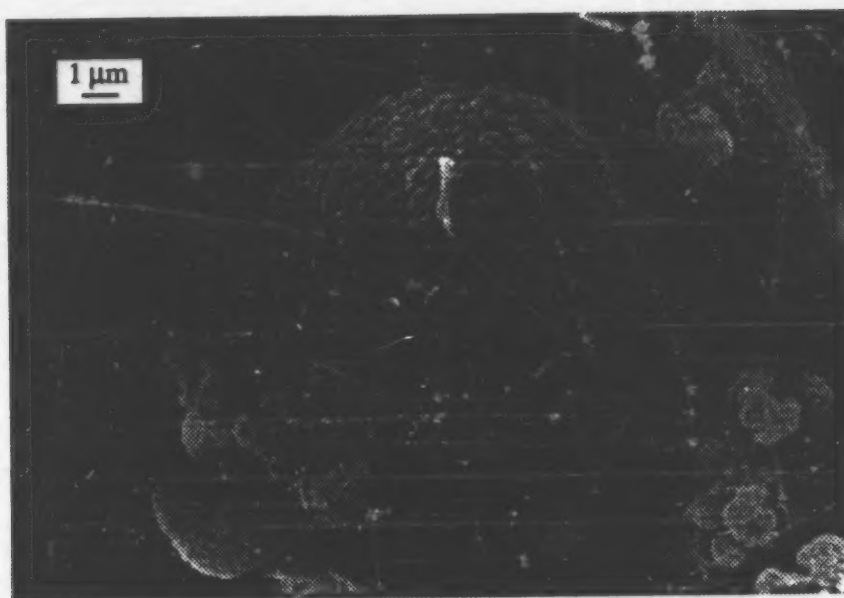


Figure 5. SEM photograph of unground LCFA slurried with $\text{Ca}(\text{OH})_2$.



Figure 6. SEM photograph of ground LCFA slurried with $\text{Ca}(\text{OH})_2$.

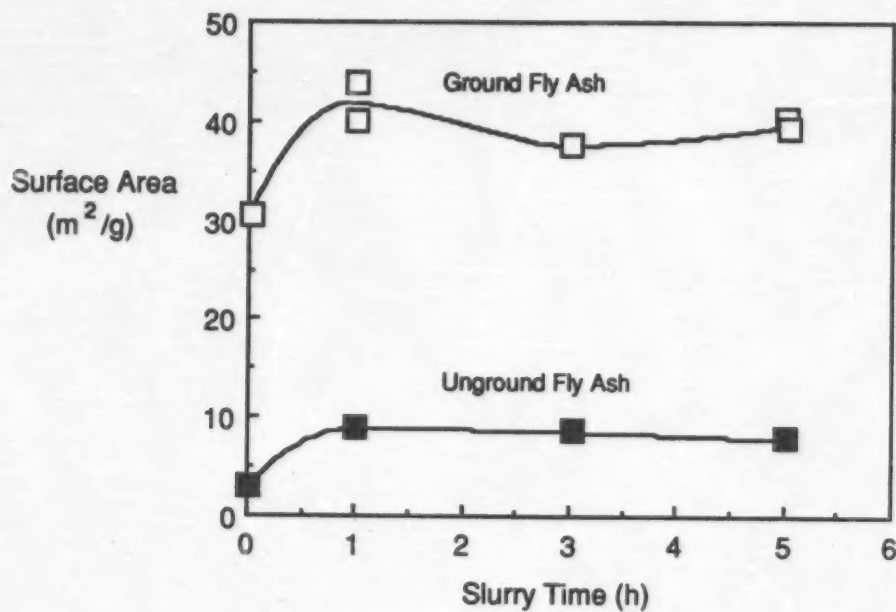


Figure 7. Effect of fly ash grinding on the surface areas of the HCFA solids.

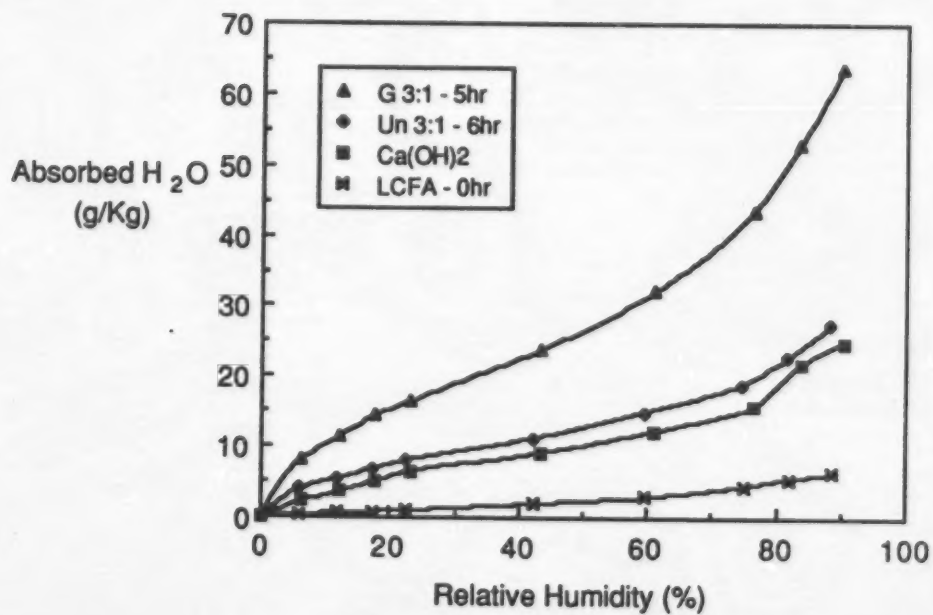


Figure 8. Water absorption isotherms for the LCFA solids. G 3:1 - 6 hr = Ground LCFA + Ca(OH)₂ (3 g ash/g Ca(OH)₂) slurried for 6 hours

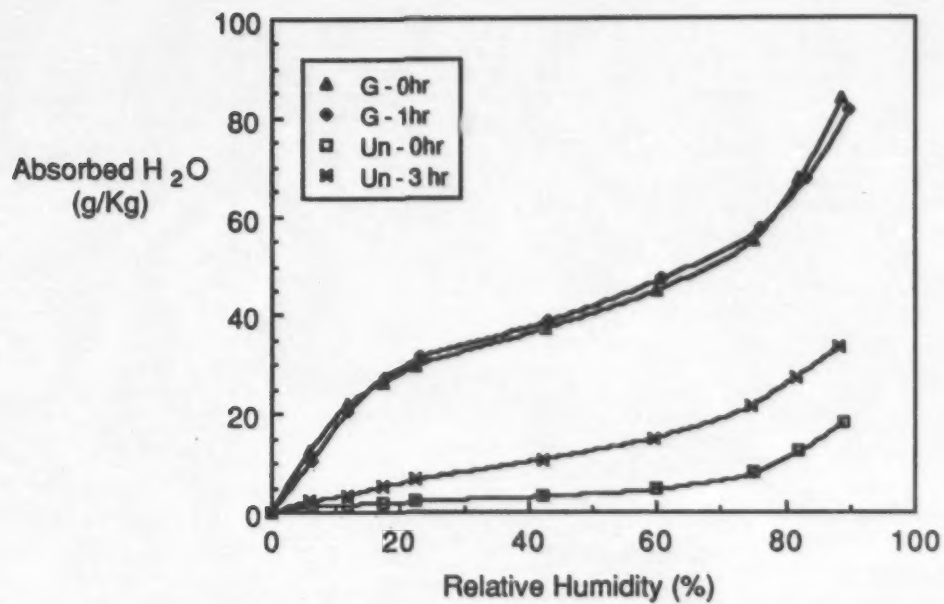


Figure 9. Water absorption isotherms for the HCFA solids.
Un - 3hr = Unground HCFA slurried for 3 hours

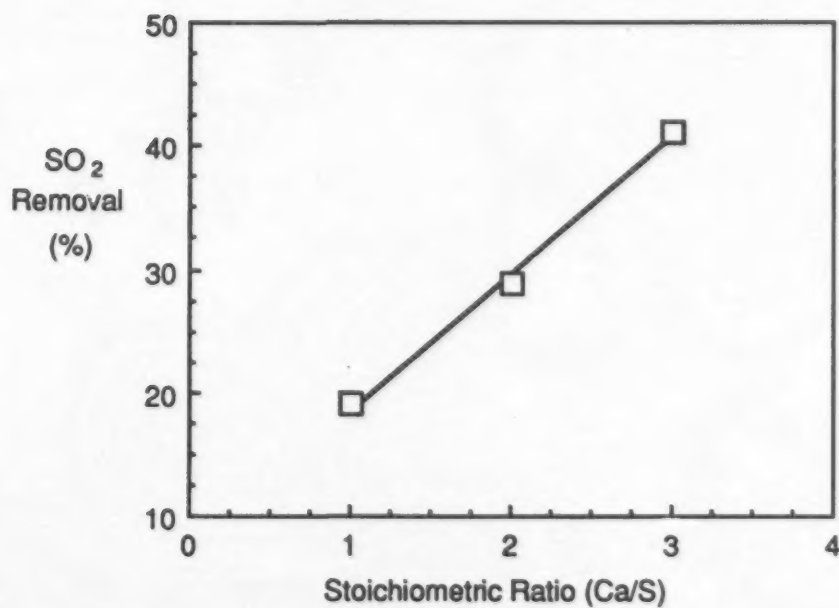


Figure 10. The reactivity of Ca(OH)₂ under duct injection conditions.

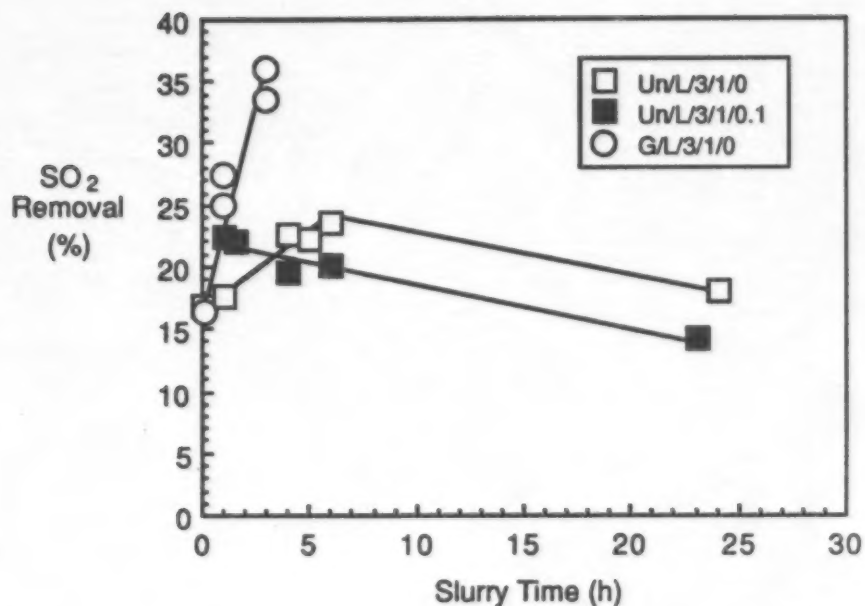


Figure 11. Effect of grinding on LCFA solids reactivity - Duct Injection. Un/L/3/1/0.1 = 3 g Unground LCFA/1g $\text{Ca}(\text{OH})_2$ /0.1 M NaOH

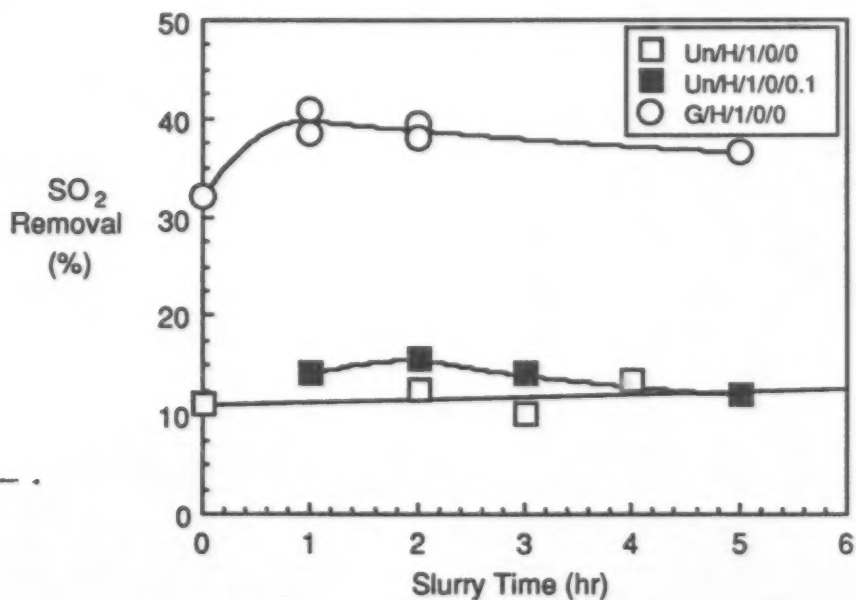


Figure 12. Effect of grinding on HCFA solids reactivity. Duct Injection. Un/H/1/0/0.1 = Unground HCFA/0 g $\text{Ca}(\text{OH})_2$ /0.1 M NaOH

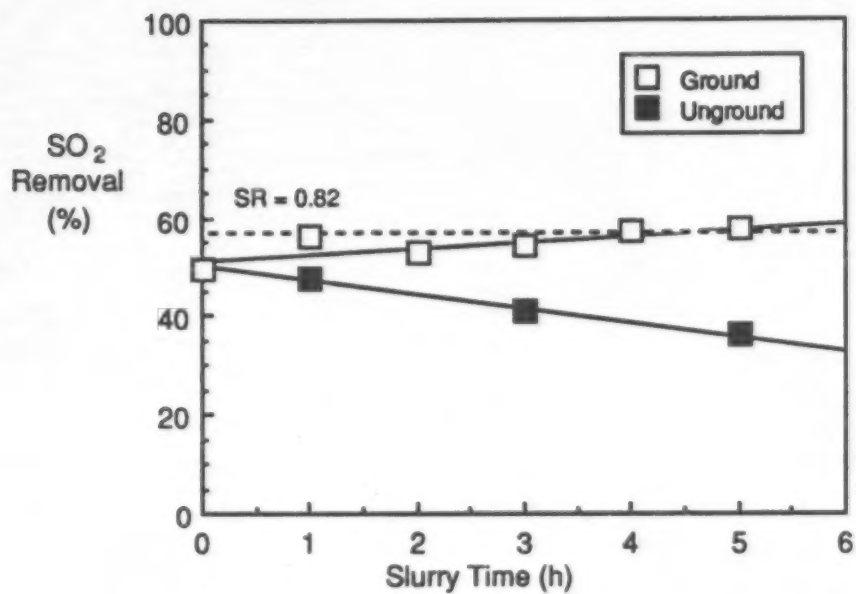


Figure 13. The effect of grinding on the reactivity of the LCFA solids in the spray dryer.

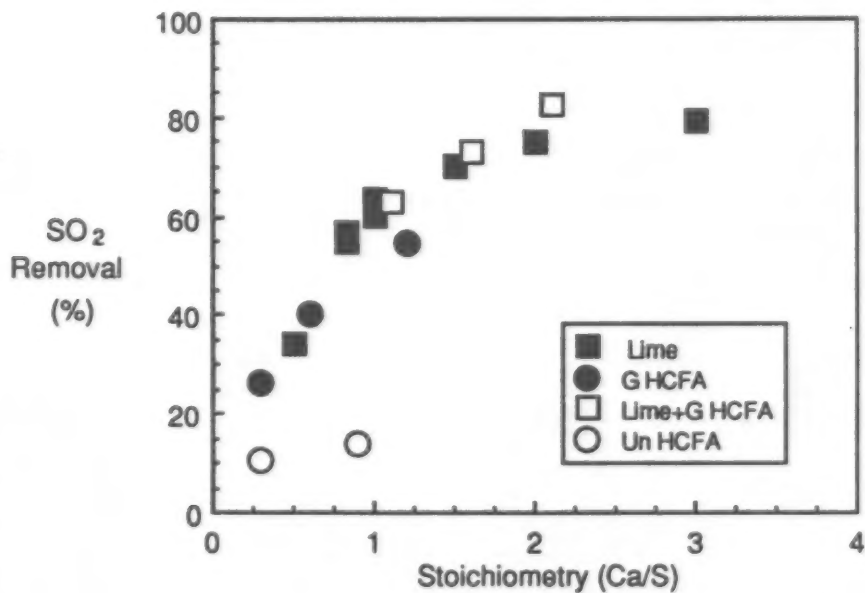


Figure 14. The effect of grinding on the reactivity of the HCFA solids in the spray dryer.

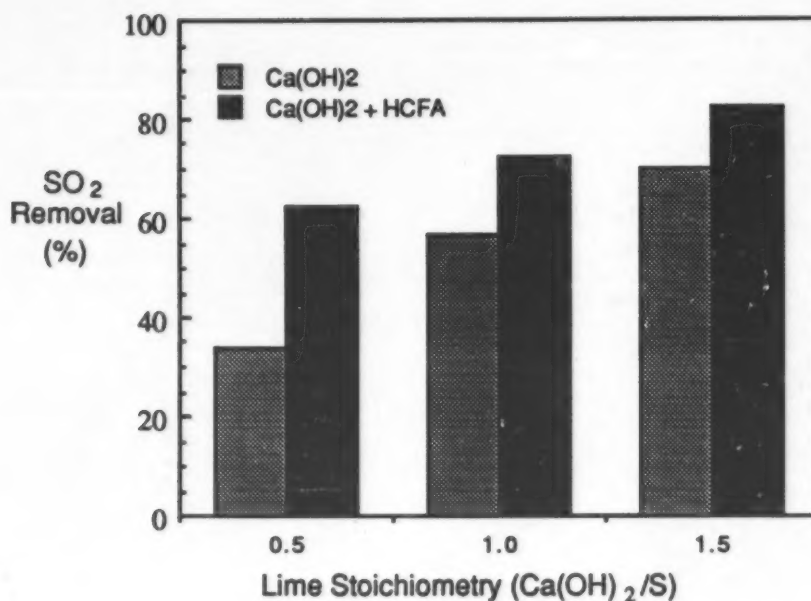


Figure 15. The effect of ground HCFA in the spray dryer. The stoichiometry for the fly ash is constant SR = 0.6.

TABLE 1. FLY ASH CHARACTERIZATION

Fly Ash	LCFA [†]	HCFA [*]
Coal Type	Bituminous	Lignite
Origin	Clinch River Power Plant	Berrenrath Power Plant
Location	USA	West Germany
Surface Area (m ² /g)	1.9	3.0
Mean Particle Size (μm) [†]	12.1	18.2
Solids Composition (wt-%)		
CaO	3.9	28.1
MgO	1.4	6.8
Na ₂ O	0.4	0.7
K ₂ O	3.0	0.5
Al ₂ O ₃	26.2	7.3
SiO ₂	55.5	20.5
Fe ₂ O ₃	8.0	35.7
Total	98.9	99.6

[†] Analyzed with XES

^{*} Analyzed with atomic absorption spectrophotometry

TABLE 2. EFFECT OF GRINDING OF FLY ASH

Fly Ash	LCFA	G-LCFA	HCFA	G-HCFA
Grinding Time (min)	0	16	0	5.2
Surface Area (m ² /g)	1.9	13.3	3.0	30.4
Mean Particle Size (μm) [†]	12.1	1.2	18.2	5.1
$D_{0.05} - D_{0.95}$ (μm) [*]	2.9-45.4	0.44-13.4	0.4-29	2.5-7.5

TABLE 3. DIMENSIONS AND OPERATING CONDITIONS FOR SPRAY DRYER-BAGHOUSE SYSTEM

Nozzle	
Type:	Sonotek ultrasonic nozzle
Frequency:	60 kHz
Maximum capacity:	7 l/h
Spray dryer	
Diameter:	0.1 m
Total height	0.6 m
Baghouse	
Diameter:	0.1 m
Total height:	0.35 m
Bag design:	high ratio/jet pulse
Total number of bags:	5
Total filter area:	0.062 m ²
Type of fabric:	needle type/polyamide
Experimental conditions	
Concentration of SO ₂ (dry gas):	1000 ppm
Concentration of CO ₂ (dry gas):	13.4%
Gas flow:	1.5 Nm ³ /s
Spray dryer inlet temperature:	150 °C
Adiabatic saturation temperature:	55 °C
Spray dryer outlet temperature:	64 and 74 °C
Gas residence time in spray dryer (NTP):	11 s
Gas residence time in baghouse (NTP):	7 s
Number of bags used:	2
Air-to-cloth ratio (NTP):	0.017 m/s

TABLE 4. EFFECT OF GRINDING AND REACTION WITH Ca(OH)₂ ON FLY ASH AND SOLIDS PROPERTIES

Fly Ash or Lime	LCFA	LCFA	G-LCFA	G-LCFA	HCFA	G-HCFA	G-HCFA	Lime
Fly Ash:Ca(OH) ₂	1:0	3:1	1:0	3:1	1:0	1:0	1:0	—
Slurry Time (h)	—	5	—	5	—	—	3	—
Surface Area (m ² /g)	1.9	18.0	13.3	55.5	2.9	30.4	41.9	14.6
Mean Size (μm) [†]	12.1	14.2	1.2	4.2	18.2	5.1	6.0	4.7
$D_{0.05} - D_{0.95}$ (μm) [*]	2.9-45.4	2.0-39.5	0.4-13.4	0.7-13.9	0.4-29	2.5-7.5	3.2-11.3	1.5-16

[†] 50% of the particles are smaller and 50% are larger than this size

^{*} The particle size range for 90% of the particles in the solid

SESSION 7C: FGD IMPROVEMENT

Chairman, Michael A. Maxwell, EPA/AEERL

ON-LINE ELECTROCHEMICAL CORROSION MONITORING IN A FLUE GAS HEAT EXCHANGER

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ABSTRACT

Advanced electrochemical monitoring instrumentation has been successfully used to monitor acid dewpoint corrosion in a heat exchanger exposed to the flue gas of a high-sulfur coal-fired boiler at Gulf Power Corporation's Scholz Steam Plant. The heat exchanger was an EPRI test facility operating in a flue gas slipstream downstream of the plant electrostatic precipitator; it was designed as the heat extraction unit of a cyclic reheat system. The primary reason for incorporating the continuous corrosion monitoring system was that, in previous tests, unexpectedly high corrosion rates had been observed at tube ends close to the side wall of the heat exchanger and the precise reasons for these high rates of attack were not well understood.

Controlled temperature weight-loss and electrochemical probes were installed in the unit in place of three of the 1-inch diameter heat exchanger tubes. The corrosion behavior of Inconel Alloy 625 over the temperature range of 120° to 260°F was evaluated at mid-stream and sidewall locations. The effects on corrosion of boiler operation, fuel composition and cleaning procedures were also evaluated.

The severe corrosion sustained by the Inconel Alloy 625 was shown to result from a combination of effects including the flue gas flow pattern, local cool-spots within the unit and locations at which ash deposits could accumulate preferentially. The relevance of this work to the integrity of flue gas equipment is that the instrumentation can provide a reliable indication of when heat exchangers are at risk from corrosion and can give an on-line assessment of cleaning effectiveness.

INTRODUCTION

Recent improvements in on-line monitoring technology allow the onset of corrosion to be detected in thin film corrosion environments which previously were difficult to appraise. Over the past eight years the Corrosion and Protection Centre Industrial Services (CAPCIS) have developed an electrochemical monitoring system for use in flues and chimneys to investigate corrosion of metal surfaces by condensed acidic species. The equipment has been successfully used in conventional dry flue gas systems (coal, oil and gas) [1-3] and in wet FGD systems (4).

The present generation of flue gas desulfurization equipment often employs some form of reheat system to raise the temperature of the gas stream after scrubbing. This practice increases the buoyancy of the gas, thus boosting the height of the stack plume and in addition, condensation in the post absorber ducts and stack is minimized. Several designs of reheater, both direct and indirect, are available but many employ steam to transfer heat from the boiler to the outlet gas, with a resultant loss in overall unit thermal efficiency. An alternative arrangement, called a cyclic reheat system, uses heat extracted from the hot incoming flue gas and transfers it to gases exiting from the absorber. This design utilizes heat which is otherwise wasted and hence avoids unnecessary efficiency losses. Cyclic reheat systems are currently in use at the Harrington Generating Station (South Western Public Service), the Romelsburg Generating Station (G.D.R.), Tokyo Electric (Japan) and the Paradise Generating Station (T.V.A.) [5].

A major difficulty encountered with the cyclic reheat approach is that of materials performance in the first-stage (heat extraction) heat exchanger. This exchanger is prone to severe acidic condensate corrosion when the tube-wall temperature is controlled below the acid dewpoint temperature. Deposit build-up on the tubes can exacerbate attack. Heat exchanger surfaces operating in a high sulfur flue gas environment, in the presence of chlorides, are exposed to potentially harsh corrosive conditions. Due to the relatively low gas temperatures encountered in cyclic reheat systems (typically 240°-310°F) and with a corresponding low heat flux across the heat transfer boundary, large areas of heat exchanger surface are required to effect reheat of the post absorber gases. The combined requirements of corrosion resistance and large surface area result in high fabrication and installation costs for a cyclic reheat system.

Of the four cyclic reheat systems cited above, only the Paradise installation has been in operation longer than a few years. Seam welded thin-walled Inconel Alloy 625 tubing was employed for the Paradise heat extraction unit but the tubes sustained severe weld/heat affected zone (HAZ) attack and bold face pitting damage after approximately 2½ years service. In the Romelsburg Station cyclic reheat system, Hastelloy C276 'finned' tubes have been installed in the heat extractor but no information is available yet on corrosion behavior.

Limited research data or operational experience exist on materials performance, tube design and fabrication, tube cleaning procedures or optimum tube operating temperature. To investigate optimum parameters for heat exchanger design and operation and to evaluate the cost effectiveness of materials for the heat extractor tube application, EPRI commissioned an extensive materials evaluation program which has been in progress for several years at the Scholz Generating Station at Sneads, Florida. Results of past work at Scholz are presented elsewhere [6-11].

Continuous electrochemical corrosion monitoring was installed on the cyclic reheat test exchanger to investigate the causes of anomalously high rates of

corrosion attack which had been observed in three previous studies. The project utilized the CAPCIS multi-technique corrosion monitor to investigate the causes of high rates of attack at locations close to the walls of the heat exchanger. Controlled-temperature tubular weight-loss and electrochemical probes were installed in the tube bundle to evaluate the corrosion of Inconel Alloy 625 over the temperature range 120° to 260°F and at two locations in the heat exchanger. In the course of the project, the separate and cumulative effects of temperature, flue gas flow distribution, ash particulate entrainment and cleaning procedures were evaluated.

ELECTROCHEMICAL CORROSION MONITORING

The cyclic reheat test facility is located at the Scholz Steam Plant of Gulf Power Corporation at Sneads, Florida. The units are fired on coal containing 2-3% sulfur. The test skid was supplied with flue gas from the Unit 2 boiler via a slipstream taken from the outlet duct downstream from the precipitator. A schematic diagram of the cyclic reheat test facility is shown in Figure 1. The general layout of the corrosion monitoring installation, featuring the cooling system, electrochemical and thermocouple lines and probe arrangement is given in Figure 2.

CAPCIS electrochemical laminar probes were employed in parallel with long-term exposure coupons, Figures 3 and 4. The individual monitoring techniques used, electrochemical impedance measurement (EIM), electrochemical current noise (ECN), electrochemical potential noise (EPN) and zero resistance ammetry (ZRA) are complementary and are useful over different ranges of corrosion activity. The EPN, ECN and ZRA data were recorded over four decade logarithmic ranges. Probe and flue gas temperature data were recorded over a range of 0-392°F.

ELECTROCHEMICAL IMPEDANCE MEASUREMENT (EIM)

The electrochemical impedance corrosion monitoring technique is based on the simultaneous measurement of a two-electrode cell impedance at set frequencies. Impedance monitoring can best be described as being analogous to the polarization resistance method used in DC corrosion monitoring techniques. The estimate of corrosion rate is based on the measurement of the charge transfer resistance (R_{ct}) which is then used in a Stern-Geary relationship [12,13,14]. The higher frequency impedance measurement gives the solution resistance, R_s , whilst the lower frequency of the second measurement is selected to assess $R_s + R_{ct}$. The difference between the readings gives R_{ct} which may be used to calculate the corrosion rate. The corrosion rate is inversely proportional to the charge transfer resistance.

ELECTROCHEMICAL POTENTIAL NOISE (EPN)

EPN is a generic term describing small amplitude random transients or fluctuations of the corrosion potential. The fluctuations are usually less than a millivolt and of low frequency, in the range 1 Hz and below. EPN monitoring may consist either of the measurement of potential fluctuations between two identical electrodes, or measurement of potential fluctuations measured with respect to a standard reference electrode. An analog instrument [15] developed at CAPCIS for on-line corrosion monitoring has been applied to flue-gas handling equipment and FGD systems. The instrument outputs the logarithm of the root mean square (rms) value of the amplitude of the electrochemical potential noise in the measured frequency range. The EPN technique provides data which can be correlated with the mode of corrosion attack, since the random fluctuations recorded are characteristic of the corrosion processes, the signatures of reaction initiation, pitting corrosion and crevice attack being especially clear. [16,17].

ZERO RESISTANCE AMMETRY (ZRA)

ZRA has been used conventionally to determine the galvanic current between two dissimilar electrodes, but may also be used successfully to determine the current between two nominally identical electrodes. It has been found that 'identical' electrodes normally have differing balances of anodic and cathodic areas and hence take up slightly different potentials. When the electrodes are coupled via the zero resistance ammeter, a measurable current will flow. Experimental evidence has indicated that the dc value of the current during active corrosion is proportional to the corrosion activity in progress on the electrodes [18].

Fluctuations in the ZRA current with time complement the information obtained by EPN and EIM measurements. Film breakdown for example, is characterized by sporadic transients in the current flow. Passive film rupture leading to pit propagation produces a larger current flow. These currents are drawn from any available cathodic sites including those of the second electrode, and the current transients are observed via the ZRA.

ELECTROCHEMICAL CURRENT NOISE (ECN)

The technique is similar to EPN, except that fluctuations in the coupling current between two similar electrodes, typically less than $1\text{ }\mu\text{A}$, are recorded and analyzed. It has been shown [19,20] that it is possible to relate current and potential noise to localized attack propensity. Overall corrosion rates from the electrochemical current noise (ECN) monitor output can be estimated from calibration data obtained from control exposures.

MULTI-SYSTEM CORROSION (MUSYC) MONITORING

The monitoring techniques described above may be used singly to monitor corrosion behavior under thin films in condensing systems. However, they are more effective when used in parallel. A monitoring and data collection system was therefore developed to utilize the response of several techniques from a single electrochemical probe [21]. The arrangement has a number of advantages when compared to the use of a collection of separate probe units: all elements are subjected to essentially identical exposure and temperature conditions, only one access point is required in the flue duct and only one thermocouple is required to monitor the temperature of the probe elements. The probes are allowed to 'condition' to a similar degree to that typical of the heat transfer tubes and their satisfactory operation is not impaired by the presence of corrosion product or ash build-up. The probes are cooled to maintain a controlled metal temperature typical of the adjacent tubes. An overall corrosion rate assessment can be obtained by combining data from the EIM, ZRA and ECN monitoring techniques [22].

The electrochemical monitors, together with probe temperature control unit, 6-channel chart recorders and data acquisition system, were located in an environmental control room, Figure 5. The exposure coupon and electrochemical probes were cooled using dry compressed air. Temperatures were maintained by analog controllers switching air solenoid valves. The two electrochemical probes were mounted in the center and at the edge of the tube bundle and subjected to a similar gas velocity to that of the adjacent tubes.

RESULTS

The specific locations of the two electrochemical probes, mid-stream in the first tube row and at the edge in the final tube row, were selected to represent the zones exhibiting least and most corrosion, respectively, in previous test runs in the cyclic reheat test facility.

ASSESSMENT OF SHORT TERM ELECTROCHEMICAL DATA

Regardless of whether corrosion was localized or general, corrosion rates contained in this section have been reported as overall (or general) rates, estimated from the relationships given earlier. The data figures, reported in this paper, represent the electrochemical signals output by the modules as a function of time. The signal distribution and statistical parameters associated with the time records are shown on the right hand side of the data figures. A step-temperature program, where the probe temperature was periodically changed to obtain a temperature/corrosion scan, was scheduled for the electrochemical monitor during the test. The temperature scan sequence was from 260° to 120°F followed by a return to 260°F in increments of 20 deg.F. This was carried out to compare the temperature-related electrochemical corrosion on the mid-stream located probe with corrosion data from the sidewall located probe.

Exposure of the electrochemical probes at temperatures typical of operational cyclic reheat exchanger surfaces (170°-240°F) allowed active corrosion to progress on the probe surfaces. For instance, data recorded at a temperature of 201°F resulted in an overall corrosion rate of 72 $\mu\text{m}/\text{y}$ estimated on the mid-stream probe, Figure 6. The effect of tube cleaning on the electrochemical corrosion process was evident from the EIM, ZRA and ECN monitor traces. Removal of the condensed acid film was indicated in the EIM trace, for instance, as a sharp increase in signal level (thereby indicating decreased corrosion) followed by a slow recovery back to the pre-wash level. This behavior was verified by the ZRA trace which mirrored the behavior of the EIM and by the ECN trace which showed greatly decreased fluctuations and mean signal level over the same period.

The edge located probe, maintained at a temperature of 237°F, recorded very high corrosion during this period, Figure 7. The decreased charge transfer resistance of 260 Ω , as observed by the output of the EIM monitor, correlated with the high ZRA and ECN monitor signals of 49.5 μA and 215 nA respectively. The overall corrosion rate calculated from the microprocessor files during this period was 940 $\mu\text{m}/\text{y}$ as compared to 72 $\mu\text{m}/\text{y}$ in the mid-stream location. The corrosion rate of Inconel 625 may be expected to decrease as the probe temperature is increased from 201° to 237°F. The greatly increased corrosion rate identified on the edge located probe is therefore directly attributable to its position in the heat exchanger. Tube cleaning was observed to have no appreciable effect on the corrosion behavior close to the tube wall at this temperature, some 2500 hours into the test run.

Corrosion behavior in the cyclic reheat test skid varied on a day-to-day and hour-to-hour basis throughout the test. This was mainly due to boiler load variation (the unit steam output generally decreased during the night) and also from the effect of coal blending. Changes in both unit load and coal blending operations can lead to variations in acid dewpoint and flue gas corrosivity, due to variations in excess air levels, sulfur dioxide, sulfur trioxide, hydrogen chloride and water vapor concentrations. A typical variable corrosion period recorded on both the mid-stream and edge located probes is illustrated in Figures 8 and 9 at probe temperatures of 263°F and 250°F respectively. The corrosion activity effectively

ceased on the mid-stream probe; the EIM monitor exhibited a low level of corrosion activity, whilst the ZRA and ECN monitor traces remained on their baselines. The overall corrosion rate decreased from 36 $\mu\text{m}/\text{y}$ to approximately 5 $\mu\text{m}/\text{y}$ during this period.

The edge-located probe exhibited a similar reduction in corrosion activity during the 12 hour period, decreasing from an overall corrosion rate of 750 $\mu\text{m}/\text{y}$ to 200 $\mu\text{m}/\text{y}$ at a somewhat lower temperature than that of the mid-stream probe. Operational data sheets from this period identified a decreased boiler steam load at 14.00 hours on 21st January. This was accompanied by a decrease in sulfur dioxide concentration in the flue gas from 1700 ppm to 1200 ppm over the following 8 hour period, after which the concentration returned to its previously seen level.

ASSESSMENT OF LONGER TERM ELECTROCHEMICAL TRENDS

Calculation of corrosion rates from the individual monitors was carried out on a daily basis. An overall rate assessment was attained by combining the statistical data from the EIM, ZRA and ECN monitoring techniques given in the data figures. The temperature/corrosion scans for the mid-stream probe location and the edge-located probe established from the test data are presented in Figures 10 and 11.

Both the mid-stream probe and the edge located probe indicated similar relative temperature/corrosion rate behavior, ie. minimal corrosion above the acid dewpoint with peak corrosion activity in the temperature range 215° to 220°F ie. 40 deg.F below the reported acid dewpoint, together with decreased corrosion activity at lower temperatures. Corrosion rate estimates from the electrochemical data, generated from both probes during the step-down temperature scan, indicated increased corrosion activity with time compared with the data generated during the increasing temperature scan.

It is clear from the similarities in temperature/corrosion behavior, established on both probes that the shapes of the corrosion curves are attributable to the condensed acid concentration and condensation rate which directly relate to the probe operating temperature. The corrosion activity experienced during the step-up temperature scans as compared to the step-down temperature scans (on both probes), is considered as arising from residual surface deposits which are not removed by water washing and accumulate during the high temperature exposure. At lower exposure temperatures (140°-185°F) such deposits are unable to adhere to the metal surfaces due to the higher acid condensation rate, these deposits are therefore more easily removed by water washing. This behavior indicates the failure of the water-wash to remove all tube surface deposits during the test.

The vast difference in absolute corrosion rates (but similar relative corrosion behavior) between the mid-stream probe and the edge-located probe is also partially attributable to differences in rates of acid deposition. Corrosion rates in condensing systems, at a fixed acid concentration, are limited by the acid condensation rate and diffusion of the acid to the active sites on the metal surface, whereas in bulk solutions, corrosion rate is less likely to be limited by this mechanism. The sulfuric acid, which is carried as an aerosol in the gas stream, is absorbed in the deposits. Acid deposition and build-up of solids occur simultaneously and differential aeration and concentration cells are initiated which prevent the formation of passive films and allow high rates of corrosion to proceed at the unprotected metal interface. These effects can cause a considerable loss in section over a short exposure period.

DISCUSSION

It is now clear that the unexplained differences in materials corrosion rates between the central section of the heat exchanger tubes and the tube sections adjacent to the sidewalls are primarily attributable to the design of this specific test exchanger. In particular, the sharp increase in duct cross section on entering the exchanger unit was responsible for an uneven pressure distribution across the tube bundle. This led to reduced gas flow over the ends of the tubes resulting in lower gas temperature and preferential solids deposition at these locations.

The corrosion rate, quantified by the electrochemical monitors, was higher adjacent the tube sheet, than in the center of the heat exchanger. This high corrosion regime was exacerbated by the inadequate tube cleaning, by an increased rate of solids deposition, and possibly by an increased rate of sulfuric acid condensation in this region. The water wash jet was unable to effectively remove deposits located at a sidewall position deep in the triangular pitch tube bundle (as was the sidewall probe located in row 7).

Test data strongly indicate that the peak corrosion rate for Inconel Alloy 625 occurs at metal temperatures in the range 215°-220°F i.e. approximately 40 deg.F below the reported acid dewpoint temperature. This temperature range corresponds to that at which corrosion conditions, determined partly by the rate of acid condensation and partly by the concentration of the condensed acid, are most aggressive. A decrease in the temperature of the Inconel Alloy 625 corresponded to a lower rate of corrosion being established due to a decrease in the concentration of the condensed acid. Over the same temperature range, higher corrosion rates were sustained on the probes which had been exposed in the heat exchanger for longer periods. This effect may be ascribed to a progressive build-up of corrosion products as the water wash system failed to remove totally all deposits from the tube bundle. These residual deposits appeared to cause depassivation of the protective oxide film and corrosion of the underlying metal surface.

Good agreement was obtained between overall corrosion rates estimated from electrochemical data and those from Battelle weight-loss analysis of heat exchanger tubes, Table 1. It is clear that the cyclic reheat exchanger system is especially prone to corrosion damage by condensed acidic species. In view of the high costs associated with such systems, it would appear desirable that monitoring instrumentation be installed to verify satisfactory plant operation. Improved life for cyclic reheaters may be obtained by more effective water washing. The possibility of using high velocity steam cleaning instead of a water wash will be evaluated in the next test period. The effectiveness of tube cleaning techniques can be assessed using on-line corrosion monitoring. Operation of the heat exchanger at reduced temperatures (in the range 170°-200°F) may reduce the condensed acid concentration and improve the expected life of Inconel Alloy 625 heat transfer tubes. However, this course of action may not be feasible on existing cyclic reheat systems if appreciable modifications would be required to provide adequate reheater surface area to achieve heat extraction from the gas.

CONCLUSIONS

1. Continuous corrosion monitoring using advanced electrochemical techniques has allowed a direct assessment of corrosion behavior in a flue gas cyclic reheat exchanger system.
2. The variation in corrosion rate of Inconel Alloy 625 with exposure temperature, has been established for the flue gas environment at the Scholz Steam Plant.

Maximum rates of 950 μ m/y at the sidewall and 95 μ m/y in the center duct were observed, approximately 40 deg. F below the acid dewpoint temperature.

3. The corrosion rate of Inconel Alloy 625 was observed to increase with exposure time. This is ascribed to the progressive build-up of deposits which were not effectively removed by the present tube cleaning procedures.
4. An increased corrosion rate was experienced on the heat exchanger tube surface close to the tube wall. This effect was primarily attributable to a decrease in the flue gas velocity and increase in particle deposition which resulted from the design of the test section and ductwork. The problem was compounded by the inability of the water wash to effectively clean those tube sections deep in the triangular pitch tube bundle.
5. The life of Inconel Alloy 625 tubes in flue gas environments may be improved by:
 - a) A more effective tube cleaning procedure.
 - b) Reduced temperature of operation (with adequate washing), but above the hydrochloric acid dewpoint.
 - c) Incorporation of design features which eliminate low gas velocity regions.
6. The capability of the instrumentation to provide a continuous indication of the effectiveness of remedial measures has also been demonstrated.

ACKNOWLEDGEMENTS

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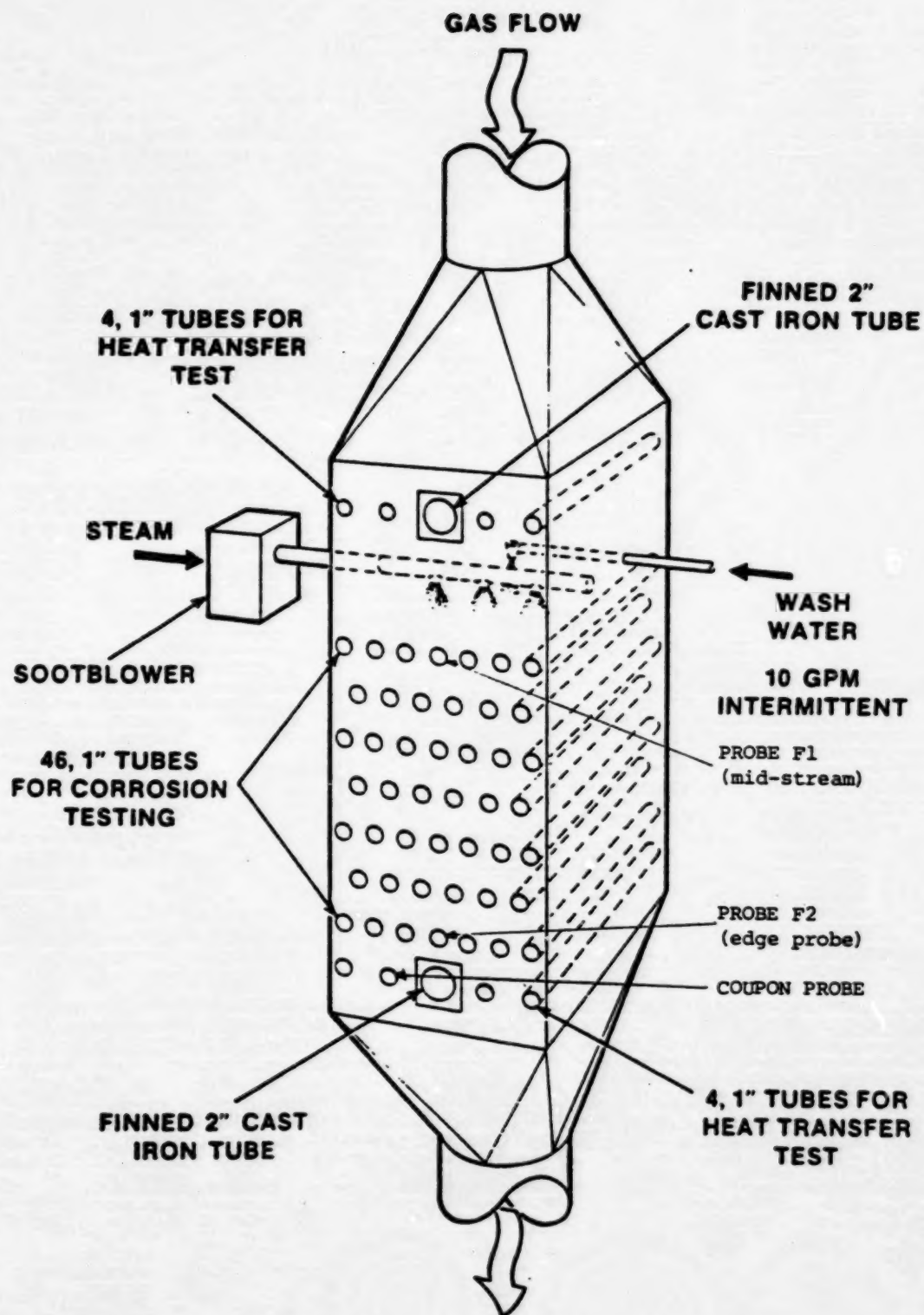


Figure 1. Schematic diagram of the cyclic reheat test facility.
(source - EPRI CS - 3700.)

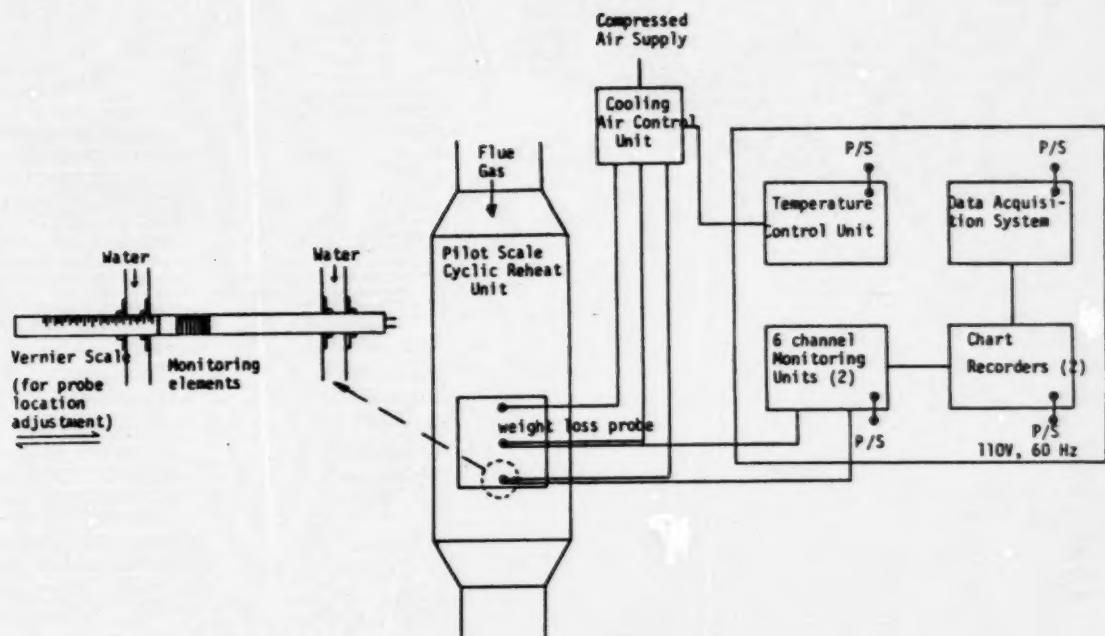


Figure 2. General layout of the corrosion monitoring installation.

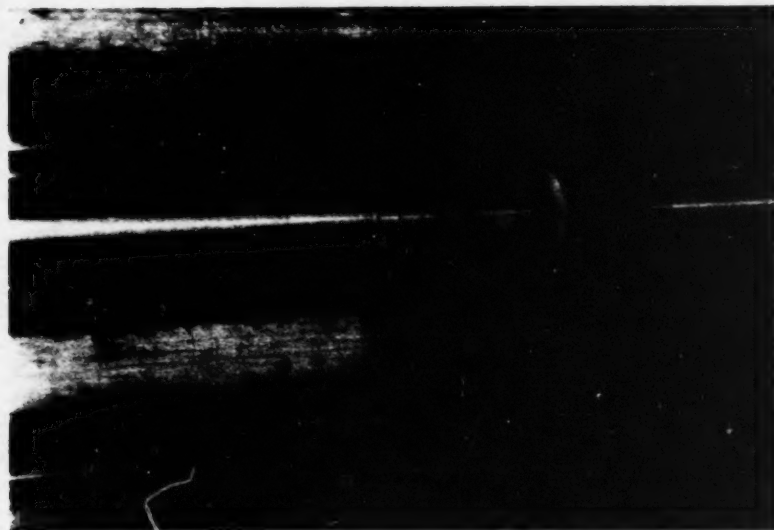


Figure 3. Cooled electrochemical probe installed in the center duct location prior to test start.



Figure 4. Variable temperature coupon probe installed in the center duct location prior to test start.

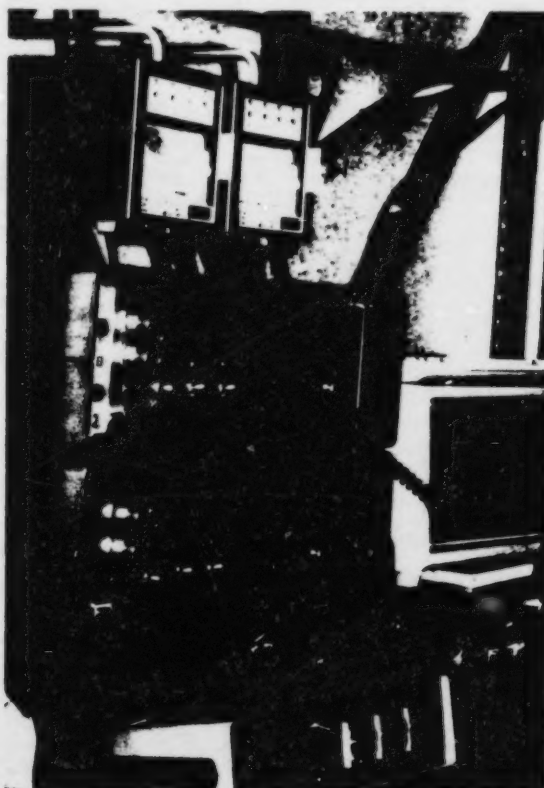


Figure 5. Electrochemical monitors, probe temperature control unit, 6-channel chart recorders and data acquisition system located in environmental control room.

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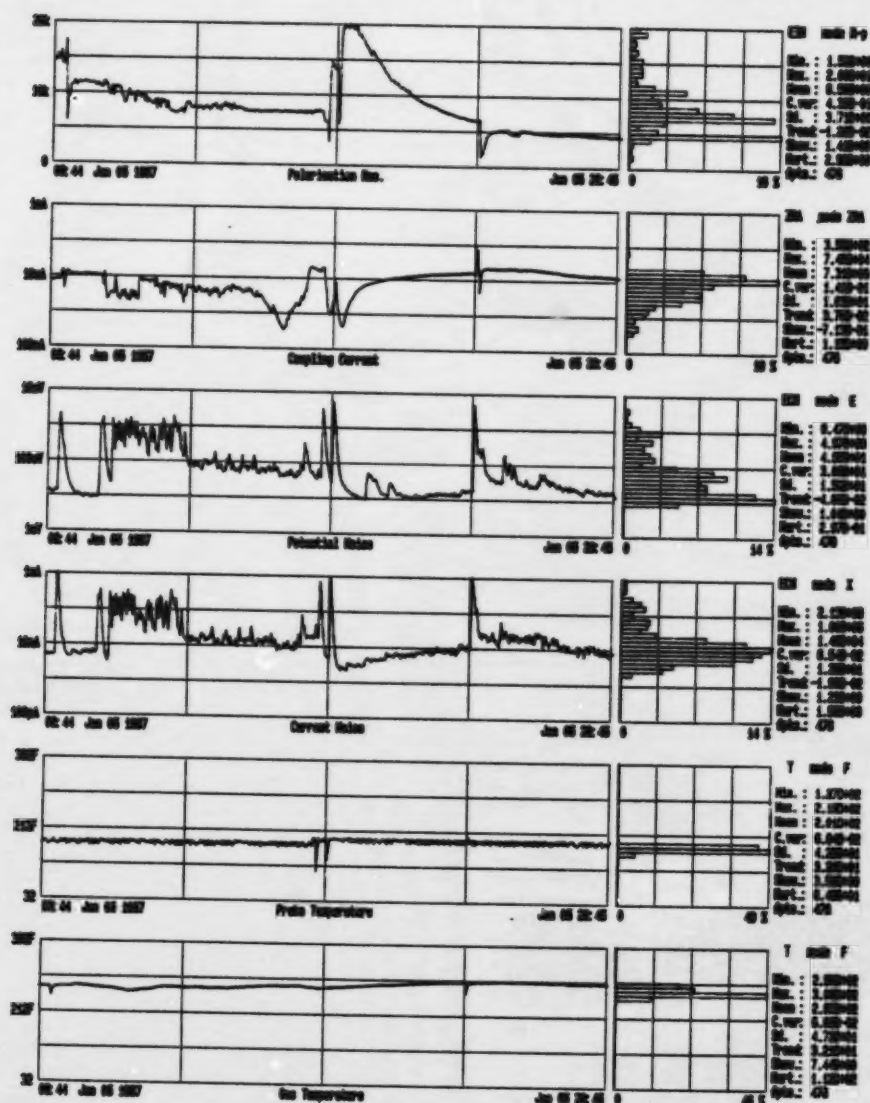


Figure 6. Electrochemical traces from mid-stream probe held at a set-point temperature of 201°F (94°C) - rate estimated as 72μm/y.

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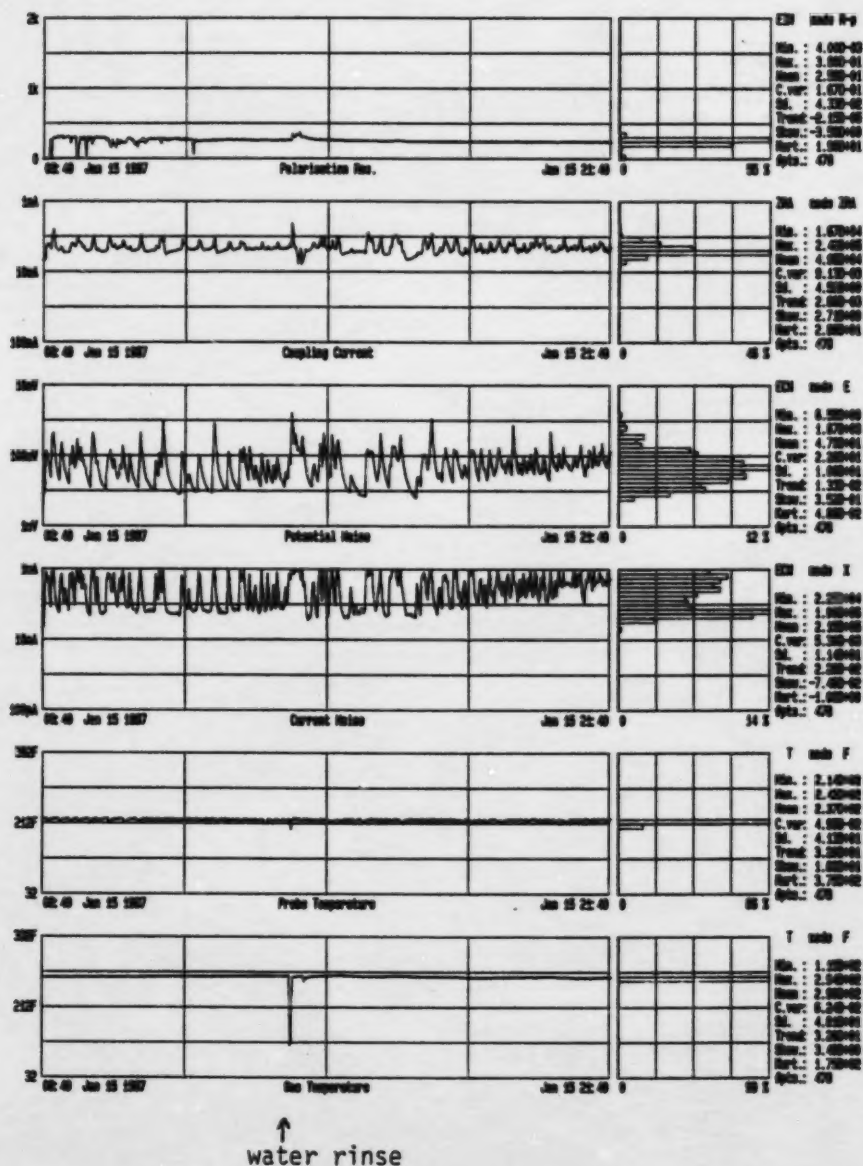
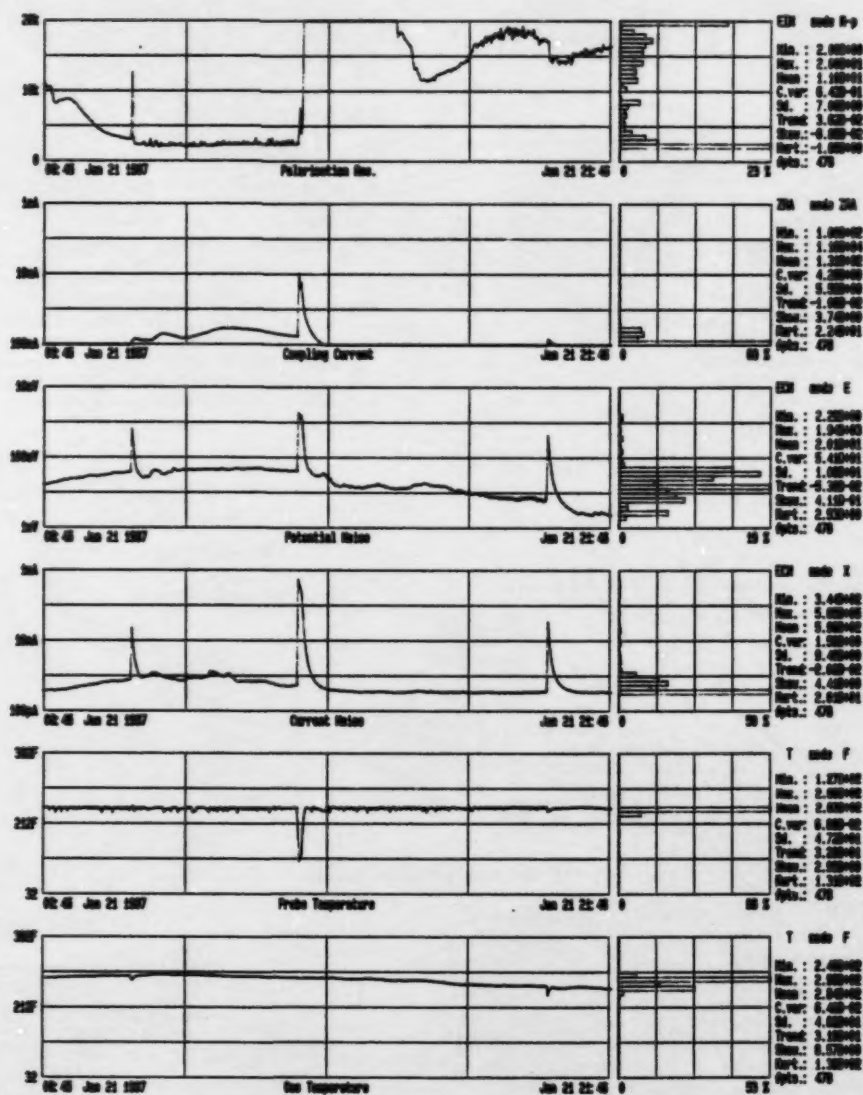


Figure 7. Electrochemical traces from edge probe at a temperature of 2370F (1140C) - high rate estimated as 940 μ m/y.



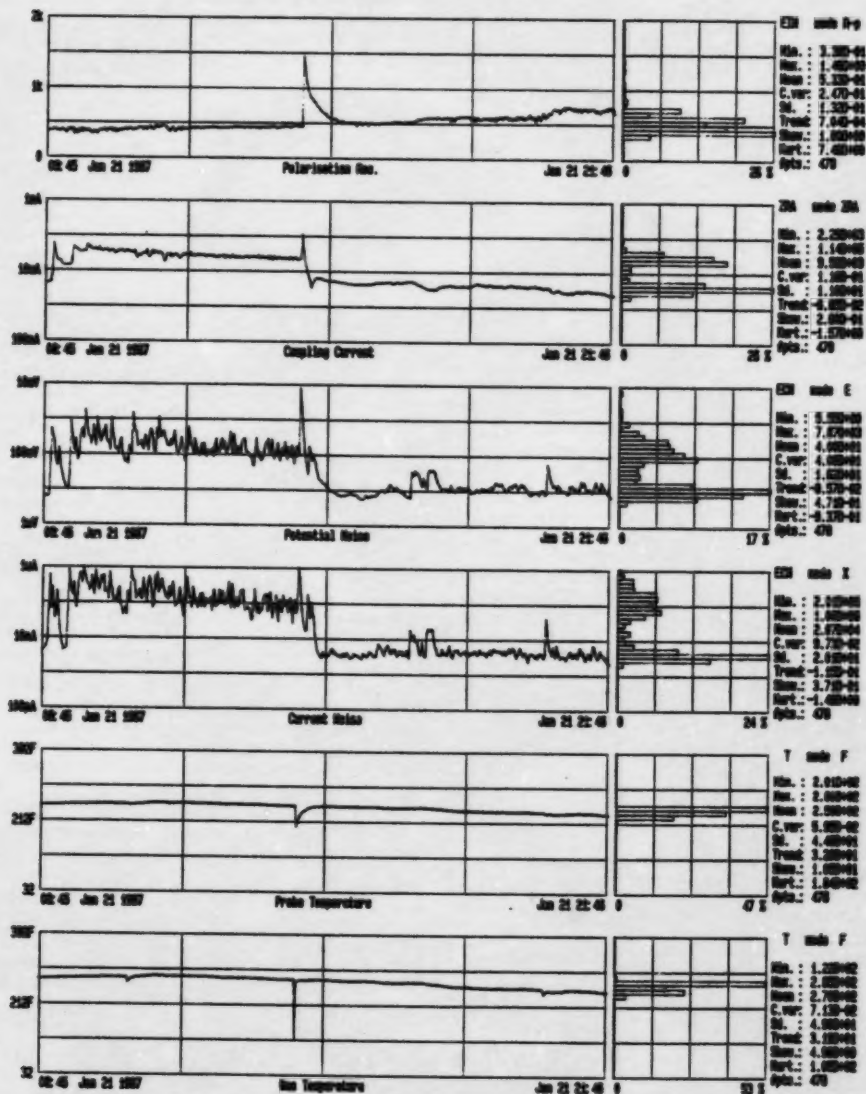
Decreasing corrosion →

Figure 8. Variation in corrosion activity on mid-stream probe - due to change in flue gas 'corrosivity' - rate decreased from 36 μ m/y to 5 μ m/y during 24 hour data file.

CAPCIS - Cyclic Reheat Test

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Decreasing corrosion
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Figure 9. Variation in corrosion activity on edge probe due to change in flue gas corrosivity - rate decreased from 750 $\mu\text{m}/\text{y}$ to 200 $\mu\text{m}/\text{y}$.

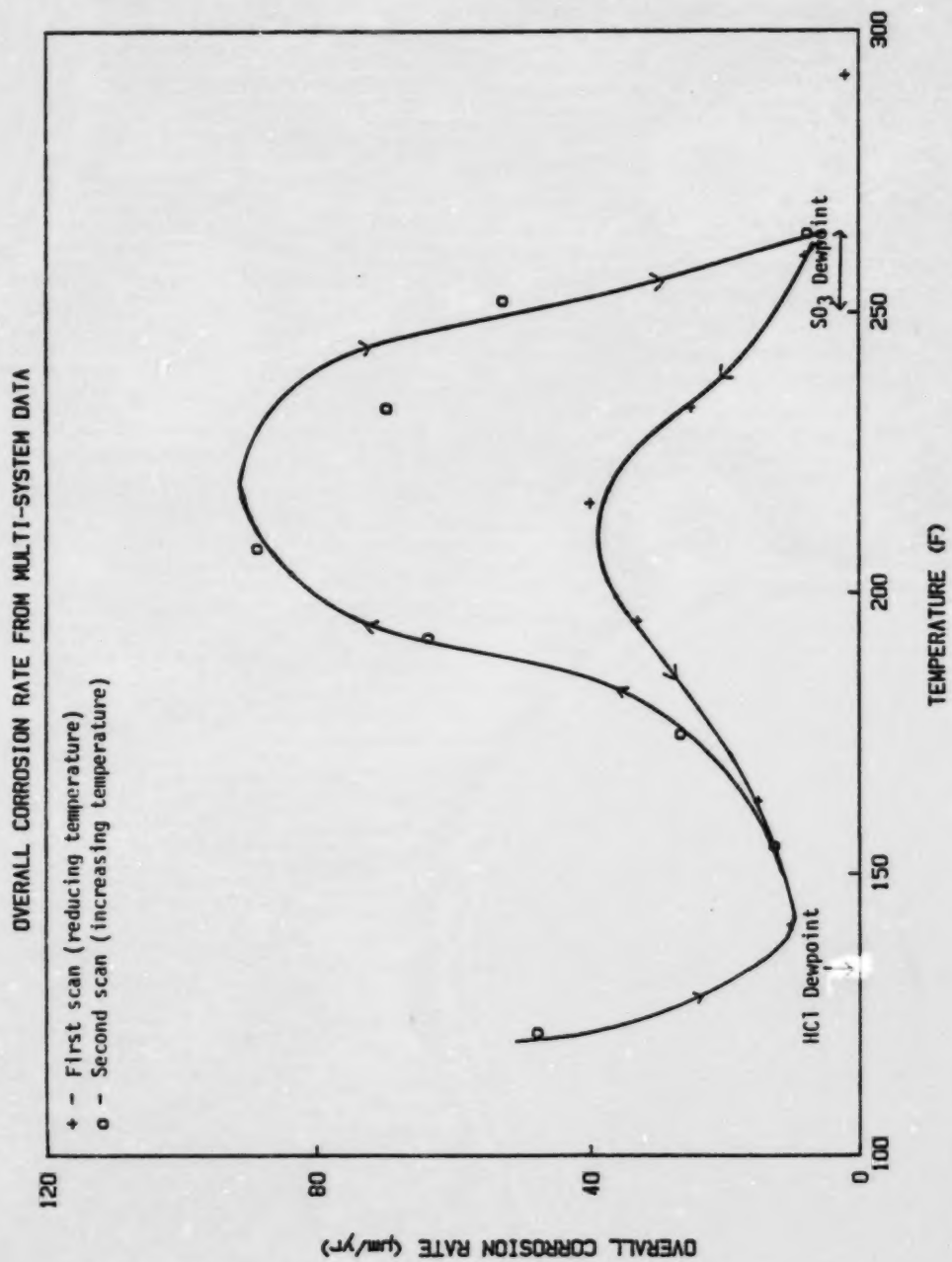


Figure 10. Overall corrosion rate from mid-stream probe - water wash.

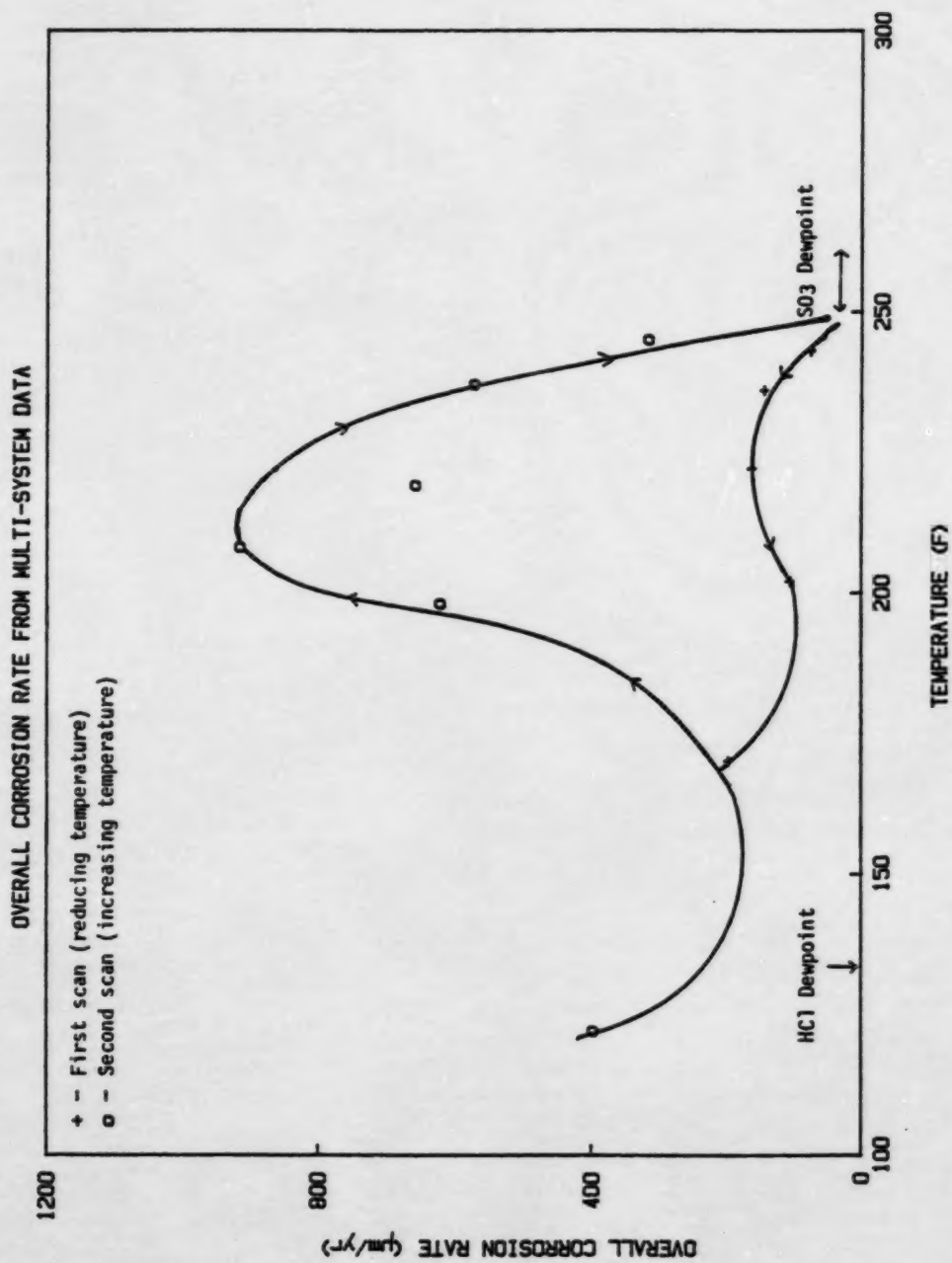


Figure 11. Overall corrosion rate from edge probe - water wash.

TABLE 1. COMPARISON OF AVERAGE CORROSION RATES ESTABLISHED
FROM WEIGHT LOSS ANALYSIS* AND ELECTROCHEMICAL MONITORING[†]

	Centre Duct Location (General Corrosion Rate)	Edge Duct Location (Localized Corrosion Rate)
Weight loss Analysis ($\mu\text{m}/\text{y}$)	79	1060
Electrochemical Monitoring ($\mu\text{m}/\text{y}$)	86	912

*Battelle Material Test Results (at 205°F, Runs 4 and 5)

[†]CAPCIS Test Results (at 205°F, Run 4).

THE EVOLUTION OF FLUOROELASTOMERIC COATINGS
FOR FLUE GAS DESULFURIZATION

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ABSTRACT

Wet scrubbed flue gas desulfurization systems are generally described, emphasizing the severity of some areas. Briefly, reasons for using protective linings and in particular, fluoroelastomers, are discussed. The importance of anticipating upset conditions when selecting coatings, the use of skilled applicators, and quality assurance requirements are discussed.

An initial first generation, fluoroelastomeric coating is described as well as successes and failures in the field. The reasons for failure in retrofit applications are discussed.

A lesson well learned led to the need to develop a second generation fluoroelastomeric coating for retrofit units. The formulation rationale behind the development strategies, that resulted in a suitable coating, are described.

Finally, field performance and laboratory studies of the second generation coating and further developments to improve field problems are discussed.

INTRODUCTION

Flue gas desulfurization (FGD) systems are subject to a variety of harsh exposures during normal operation including high concentrations of acids, abrasion and erosion, thermal gradients, wet/dry/hot cycling, and flexing movements. The combinations of conditions can rapidly degrade metallic, hydrocarbon, and silicious materials.

Due to their inherent stability to aggressive chemicals, especially acids and high temperatures, fluoroelastomers were a natural choice to formulate into coatings designed to protect FGD components. Fluoroelastomer coatings were introduced to the power industry for use in FGD systems after years of successful FGD applications of fluoroelastomers as molded articles such as expansion joints.

The evolution of a second generation fluoroelastomer for retrofit wet scrubber systems is described as well as the successes and failures of a first generation fluoroelastomer developed originally for new construction.

BACKGROUND

The enactment of clean air legislation during the past 20 years forced electric utilities to adopt new technologies designed to reduce SO_2 emissions from flue gas generated by coal-fired boilers. A variety of FGD designs exist but common systems scrub exhaust gases by wet methods.

The design and operating conditions of wet scrubbers were thoroughly described in recent publications (1, 2). The actual designs, and service and operating conditions can vary so much that each facility may be functionally unique. Conditions will vary from point to point within any system. A simplified plant schematic is shown in figure 1.

In wet scrubbing systems quantities of unscrubbed gases, at 280 to 360°F, may frequently be bypassed directly to the exhaust ductwork to be mixed with scrubbed gases upstream of the scrubber. The composition of flue gas condensate can vary widely but common components are oxides of sulfur and nitrogen, chlorides and fluorides, calcium and magnesium, and entrained flyash. Berger et al characterized the wide range of condensate constituents (3). Ideally, most of the hot, acidic gases pass through the inlet duct to the scrubber where intimate contact is made with mixtures of water and alkaline materials. The scrubbed gases contain significantly reduced concentrations of corrosive species and have cooled to 140°F or lower; hence, acidic condensation may occur when the gases enter the absorber outlet duct.

Upstream of the outlet duct, in the mixing zone, temperatures normally range from 125 to 140°F and may exceed 400°F during unit excursions. The outlet duct/mixing zone area is frequently described as the most corrosive portion of wet FGD systems. Corrosion rates "15 times higher than anticipated" have been reported (4). A recent author typified the outlet and chimney areas as experiencing the "highest temperatures, strongest acids, and most abrasion, plus flexing/vibration"... "and fluctuating flue gas flows" (2). Significant concentrations of SO₃ may remain in the scrubbed gas and consequently raise the acid dew point temperature high enough that utilities can not afford to reheat the scrubbed gases enough to avoid acidic condensation (2).

The mixed gases enter the main ductwork then the breechings prior to exiting to the chimney. In the breechings temperatures may range from 200 to 360°F during normal service and the components may be exposed to scrubbed and bypass gases. Finally, in the chimney the rising gases may cool enough to create further dew point condensation, with temperatures of 150 to 200°F. In tall chimneys vibrations, and physical and thermal stress/strain may be severe (2).

PROTECTION FOR FGD COMPONENTS

Due to the cost of constructing, operating, and maintaining wet FGD systems low cost carbon steel is frequently used as a major material of construction. However, unlined steel rapidly degrades under the conditions present in wet FGD units. Efforts to extend the service life of FGD components resulted in the use of a wide range of protective linings.

Hydrocarbon based linings perform well and are economical choices for protection in some areas. Silicious linings also perform well in specific areas; however, their use is limited by their susceptibility to attack by fluorides and by their weight. Ideally, in order to protect mild steel in the more harsh environments, a lining should be thermally stable, resist thermal shock, resist strong acids (particularly mineral acids), be moderately flexible, abrasion resistant, and have excellent chemical resistance. Fluoroelastomeric linings satisfy all of the above criteria.

The applicability of fluoroelastomer coatings for FGD is well described by Montle: The areas of use inside FGD environments that have demonstrated suitability for fluoroelastomeric linings include the absorber outlet ducts, which are characterized by thermal gradients, high acid environments, and abrasion, the mixing or bypass zones, with their intermittent wet/dry/hot environments, abrasion and strong acid conditions, breaching, which is similar to the mixing zone environment, with substantial movement; the main large ductwork with its considerable

flexing movement; the turning vanes, subject to severe abrasion; various internal bracing subject to abrasion, flexing and difficult application due to complex geometry; and steel lined chimneys where low weight per square foot of fluoroelastomer linings have shown significant advantages (5).

However, Fluoroelastomers are not a cure all for all aggressive FGD areas. Where the normal service temperatures exceeds 400°F or in the alkaline conditions that may exist in scrubbers fluoroelastomers are not suitable.

QUALITY CONTROL: KEY TO PROTECTION

The continued operation of an FGD system is dependant upon several factors that extend beyond the selection of a lining material resistant to the hot, corrosive flue gases. It can not be stressed firmly enough that successful performance of the ideal lining requires good engineering design, appropriate environmental field conditions during lining application, proper substrate preparation, well trained applicators using recommended equipment, and particularly quality assurance during surface preparation and application (1, 2, 6).

Lining materials, available to protect FGD components, should be considered during the design stages of the system in order to assure optimum lining lifetime, minimum application problems and costs, and maximum performance. In STP 837 ASTM recommended that the design and fabrication of the components should consider the physical performance limitations and application requirements of the lining (1). Relationships considered should include:

- 1) Lining strain and deflection limitations when determining the rigidity of the supporting substrate.
- 2) Providing access to all interior surfaces to permit surface preparation and lining application.
- 3) All welds should be continuous, and the coating manufactures specifications concerning weld preparation should be adhered to.
- 4) Internal stiffeners should be simple closed shapes to permit lining application, and angled or complex shapes avoided.

When the lining is applied, environmental conditions necessary for proper installation must be provided. Possible considerations are heaters, that exhaust clean gases, for applications in cold weather in order to avoid dew point condensation and provide sufficient ambient heat to cure the coating. Provisions for getting the application equipment close to the job should be made. Ideal coating performance often depends upon the availability of ideal application conditions.

Currently available coatings for very aggressive exposure conditions require that particular attention be paid to proper cleaning and blasting of the substrate.

Particular attention should be paid to all welding requirements and final preparation of the welds. In all cases the substrate should be blasted to white metal cleanliness (SSPC SP-5 or NACE #1). The lining manufacturers recommended blast profile and suggested blast media should be closely adhered to. Fluoroelastomeric coatings generally depend upon a high profile of 4 mils (nominal) to develop physical adhesion. This is illustrated in Table 1 which presents dry thermal exposure data generated from a fluoroelastomer formulation applied at two film thicknesses over carbon steel. The substrates had either the specified blast profile of 4-5 mils or an inadequate profile of 2-3 mils. The greatest film thickness (35-40 mils) had lost most of the initial adhesion within 138 days when applied over an inadequate substrate yet the adhesion was maintained over the specified profile even after 170 days of exposure.

Essential to achieving the recommended surface preparation and successfully applying a lining is that the applicators be highly skilled and well trained in the use of the required equipment.

Ellis and Moser described quality control as the weakest link in the chain, ultimately leading to FGD failures (6). The most efficient design is nearly worthless if at some point during fabrication or installation designs are not adhered to or materials are installed improperly. It is essential that the process be strictly monitored and documented at all stages by qualified, reliable inspectors.

Finally, conditions exceeding component/system designs must be anticipated and considered when selecting an FGD lining. A hydrocarbon based lining performing well in an outlet duct under design conditions at 140°F, could fail catastrophically during an excursion where temperatures could reach 450°F. A fluoroelastomer lining that had performed well in a breech area for five years was reported to fail rapidly, on the duct floor, when there was an unexpected alkaline absorbant spillover. Perhaps these failures could have been avoided if the upset conditions had been considered when selecting the linings.

FIRST GENERATION FLUOROELASTOMER

An early fluoroelastomer coating introduced to the FGD market enjoyed mixed successes and failures. That coating will be referred to, in this paper, as the first generation fluoroelastomer. The successes were generally in new construction situations in which long time periods elapsed

between the coating application and the plant start up. Most failures were associated with re-trofit applications where the units were put back into service quickly.

A successful application was in 1972 in a 4000 megawatt coal-fired power plant. The linings of the concrete chimney and entry ducts were coated with 30-40 mils of the fluoroelastomer during the initial construction of the FGD system. Ten years later inspections revealed that the coating was in excellent condition and an additional ten years of service life were predicted.

The first generation lining was applied to the ductwork of a new FGD unit. During initial phases of the unit start-up the lining was exposed to low volumes of low temperature flue gas prior to exposure to full service conditions. The lining was in excellent condition until exposed to the extremes of a high pH lime slurry spillover five years later.

Retrofit FGD applications proved to be much more demanding of the first generation lining. The fluoroelastomer was applied under close supervision, to the mixing zone associated with a closed loop scrubber. Two weeks of curing were permitted under ambient conditions prior to start-up. All preparation and application requirements were satisfied. The service conditions were not excessive with an average temperature of 135°F, a few excursions to 280°F, and high concentrations of halides. Yet, after six months of service severe blistering was reported in the lowest portions of the duct.

Similar failures were reported in numerous retrofit applications. Generally, the failures involved blistering or large scale delamination of linings in outlet ductwork and mixing zones.

Blistering was responsible for lining failure in most cases. The possibility of multiple causes for blistering was indicated from field reports of quality control activities. A "solvent entrapment" test was required before proceeding with the application of successive coats. This involved raising the temperature of an area of the coating, using a heat lamp, to 300°F, over a period of five minutes. If no blisters appeared, the lining was judged to be acceptable for recoating. The appearance of blisters during the test did not correlate very well with actual field performance. Blistering was a frequent mode of failure for applications that passed the test.

Three mechanisms were identified as responsible for the blistering failures. Possible causes were solvent entrapment, osmotic cell formation, and the rapid evolution of water or HF as a by product of the cross-linking of the fluoropolymer. A contributing factor to the variations in the

performance of the fluoroelastomer was attributed to specific differences between application time schedules and start-up conditions.

New construction applications generally provided relatively long periods of time between successive coats and often long final drying times prior to unit start-ups. This provided ample time for the solvents to escape and the coating to cross-link. The cost of downtime in retrofit situations necessitated minimum recoat and final dry times before start-up. Short time periods coupled with exposure to rapidly increasing start-up temperatures may have resulted in blistering as the rate of solvent volatilization exceeded the diffusion rate through the coating film. The phenomenon would have been accentuated in a fluoropolymer as highly cross-linked as the first generation lining.

Osmotic blistering was also a possible cause of blister formation. In some field failures, water containing dissolved salts was discovered when the blisters were opened. The presence of residual hydrophilic solvents could have accelerated osmotic blistering as demonstrated recently by Storfer and Yuhas in their investigations of mechanisms of blister formation (7).

In most cases of field failure due to blister formation, no evidence of water or salts was found beneath the blisters, and evolved vapors from laboratory tests revealed the vapor to be alkaline. Hydrogen fluoride may not have been generated in some cases. Whether the evolution of HF or water was responsible was not confirmed. However, as with entrapped solvents blisters could have been caused by small amounts of HF being generated at a rate greater than its reaction rate with the coatings acid scavenger; or by water evolved, from the neutralization of HF by the acid scavenger, at a rate in excess of the diffusion rate of water through the coating film. Evidence presented in an EPRI study at R.D. Morrow station lends some support to this theory. In that study generalized corrosion was discovered beneath the dry blisters (8). The type of corrosion was attributed tentatively to HF and appears to be consistent with the type of general corrosion attributed to fluoride ions (4).

The massive delaminations, of the first generation fluoroelastomer lining, that were discovered in a few cases of failure in FGD units can be attributed to two causes. They are the lead oxide acid scavenger and the highly cross-linked nature of the lining. Only a small degree of cross-linking is believed to occur in short time periods at ambient temperatures. At elevated service temperatures sufficient additional cross-links probably form until the coating becomes brittle. Coupled with the shrinkage that generally accompanies increasing cross-link density and evaporation of

solvents the lining probably lifted directly off of the substrate. Finally, lead oxide is reported to detract from the adhesion of fluorocarbon elastomers to metal and impart poor heat aging properties (9).

Beyond the field failures that plagued the first generation fluoroelastomer lining their were numerous other complaints and problems experienced in the field.

The time required for careful multi-coat application and final drying was excessive considering the cost of plant downtime. Following the time intensive application and dry time schedule a clumsy thermal cure cycle was required. The schedule was difficult or impossible to implement. In the can the coating exhibited rapid, extreme, hard settling.

All of the evidence pointed to an urgent need to reformulate the coating to meet the needs of the field for retrofit wet FGD systems.

FORMULATING THE SECOND GENERATION

In a recent study, funded by the Electric Power Research Institute, White and Leidheiser showed that films of specific fluoropolymer and acid scavenger formulations did not provide adequate protection in acidic exposures (10). Normally, a fluoroelastomeric coating consists of fluoropolymer resins, acid scavengers, fillers and reinforcing agents, thixotropes, cross-linking agents, and solvents. As discussed by Tuckner, the selection of reinforcing agents and fillers can readily effect the performance of coatings (9). The exact proportions of each component is balanced to meet the application and performance requirements for the coating. This serves to underscore the problems noted here with the first generation fluoroelastomer.

In response to numerous field complaints and failures an extensive effort was mounted to develop an improved fluoroelastomeric lining, the second generation.

Previous unsuccessful fixes applied to the first generation fluoroelastomer lining emphasized the need to totally reformulate the coating.

The properties desired in the new coating were:

- 1) Good thermal stability (continuous performance at 350°F, with excursions to 500°F)
- 2) No blistering on plant start-up
- 3) Fast recoat time (6-8 hours between coats at 75°F)
- 4) High film build (125-200 microns dry film per coat)
- 5) Good application characteristics by airless spray

- 6) Long pot life (>8 hours)
- 7) More competitive costs (thinner films, lower material costs)
- 8) Flexible and elastomeric
- 9) No toxic lead compounds
- 10) Good shelf stability (no hard settling)

The first generation coating had a one hour potlife. Excessively high concentrations of a polyamine cross-linking reaction were responsible. As stated earlier, this was implicated in blistering problems as well. In a copolymer based coating, such as the first generation coating, a high cross-link density was necessary in order to rapidly achieve reasonable mechanical properties (hardness, abrasion resistance) under room temperature curing conditions. In order to achieve acceptable mechanical properties at reduced cross-link density a higher molecular weight terpolymer (composed of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene) was chosen. The resulting coating was excessively viscous and exhibited poor spray characteristics. Finally, a composition including a minor concentration of copolymer proved successful.

Blocking the polyamine chemically further increased the potlife. In this form the polyamine was prevented from participating in cross-linking reactions until unblocked by reactions occurring during and after application.

Decreased recoating time and a shorter final drying time were accomplished concurrently with the change to terpolymers and reduction in cross-link concentration. Terpolymer compositions can form coating films by solvent evaporation and with cross-linking reactions occurring at much reduced rates the problem of solvent retention was significantly reduced.

The selection of solvents was also investigated. Solvent choices were limited to lower molecular weight ketones and esters by the solubilities of the resins. However, blends of primary solvents were successfully chosen to balance sprayability, dry spray tendencies, rate of drying, and viscosity. The physical characteristics of various blends of solvents pointed to a blend of methyl isobutyl ketone and n-butyl acetate that was a compromise between polarity, evaporation rate, and solubility. Fast evaporating methyl ethyl ketone (MEK) was investigated closely due to its ability to readily dissolve the resins; unfortunately, when the coatings application properties were evaluated much dry spray resulted. Earlier experiences with an MEK borne fluorocarbon FGD lining material resulted in excessive dry spray and numerous pinholes. The FGD unit where it was applied was forced to shut-down within 6 months due a catastrophic lining failure. A section of the pinholed MEK borne coating is contrasted with the second generation lining in figure 2. The bright pinpoints of light are pinholes.

Polyamines are believed to cross-link fluoroelastomers by dehydrofluorination. Although the HF is present in very minor concentrations, as discussed earlier in this paper, problems can result; consequently, fluoroelastomers are formulated with acid scavengers that serve as weak bases to neutralize the HF. Lead oxide, in the first generation lining, was chosen for reasons of its insolubility in acids. Lead oxides in fluoroelastomer coatings are reputed to be responsible for hard settling tendencies, poor adhesion, and poor thermal stability. Thermal analysis of the first generation lining is shown in figure 3 with a DSC curve. The analysis reveals that even after long cure times, samples which contain lead oxide undergo a substantial exothermic reaction when heated above a threshold temperature. This runaway reaction can cause the normally rubbery lining to become brittle and hard. A non-toxic metal oxide acid scavenger was chosen for the second generation lining.

Properly formulated fluoroelastomers retain their elastic properties for long periods at elevated temperatures as depicted in figures 4 and 5. Laboratory investigations of the adhesion of fluoroelastomer coatings to mild steel exposed at elevated temperatures revealed that some reactions occur at the metal/coating interface. The degradative reaction causes a gradual loss of adhesion at temperatures lower than those required to degrade the linings elasticity. This phenomenon was also observed with fluoroelastomers formulations coming from other laboratories. Changes in adhesion to mild steel as a result of dry thermal exposure are presented in figure 6.

Consideration of the elastomeric properties of free films and the useful temperature range of the second generation fluoroelastomer resulted in the recommendation of a continuous exposure temperature of 350°F. Improvement in the interfacial properties is an obvious area for further improvement. To date, experiments have investigated a variety of approaches, from different types and concentrations of acid scavengers to metal primers without finding an acceptable solution.

Atlas Cell studies of metal primers revealed that an improvement in performance occurred in the immersed regions of the second generation lining. Unprimed linings were shown to blister in liquid exposed areas about 50% of the time and showed general loss of adhesion after around 3 to 4 months of exposure to 5% sulfuric acid with 0.5% hydrochloric acid at 150°F. Treatment of the blasted substrate, with a metal primer solution, prior to coating was demonstrated to essentially eliminate the blistering with little change in adhesion.

Table 2 compares some of the properties of first and second generation fluoroelastomeric linings.

SECOND GENERATION FIELD TRIALS

Field performance was the major goal of the second generation lining development studies. Laboratory performance testing had demonstrated superior physical and chemical properties. Field trial applications took two general forms, on-site test patch applications under field conditions, and FGD exposure of panels, man-way doors, etc., that were prepared under laboratory conditions.

A review of retrofit and maintenance applications illustrates the success of the new lining material.

The oldest application was in an outlet duct downstream of a limestone absorber unit in a lignite fired power plant. The environmental conditions at the time of application were poor, with repeated work stoppages due to rain and dew point problems. The fluoroelastomer was applied at 20 and 40 mils to the walls, ceiling, target plate, and roll plate. The coating was exposed to flue gas believed to consist of H_2SO_4 , HCl , HF , other HX , SO_2 , and SO_3 (all at unknown concentrations). Normal operating temperatures were from 140 to 180°F with a half dozen extended exposures to unscrubbed by-pass gases at 350 to 400°F. At the two year inspection the lining was in excellent condition with some blistering on the roll plate. Analysis of the failed areas indicated that immersion-like exposure was the probable cause of the blistering. Subsequent to this application recommendations were changed to include a metal primer application to areas suspected as being immersion-like.

Panels and man-way doors coated with 35 to 40 mils of the new lining material were prepared on site and exposed at various locations in the ductwork and breech of a closed loop FGD system using limestone absorbant. The 3'X 3' panels were exposed at the reheat air entry sites (400°F), the mixing zone (140-250°F), and bypass entryway (330°F). The flue gas typically contained 3500 ppm of sulfates, chloride ions at 200-10,000 ppm, and fluoride ions at 100 ppm, at a pH of 1.6. After nearly two years of exposure, the new fluoroelastomeric lining was reported to be in excellent condition. Previously an aluminum silicate cementitious lining and a competitive fluoroelastomer had failed rapidly.

A third application was to compressor silencers, with normal operating temperatures of 280 to 300°F and excursions to 350°F. Exposure was to boiler flue gas, diesel fuel, polythiol acids, and hydrocarbons. Previously 316 stainless steel had failed here due to corrosion fatigue. After three years exposure, performance is excellent.

The lining failed in hot, alkaline ($\text{pH} > 9$) environments, as was expected. In one case, the lining was overheated ($> 600^\circ\text{F}$). The hardened and blistered material was judged by the customer as a failure. Failure analysis revealed however, that the underlying metal was still protected with no blistering to the substrate. The performance was determined to be a definite success.

POSSIBLE THIRD GENERATION LINING SYSTEM

Although the second generation fluoroelastomeric lining has been demonstrated to have superior performance than earlier products, there is still room for improvement. In particular, the maximum service temperature needs to be extended. This may be accomplished by a new metal bonding agent or primer coating. The solvent combination present in the material should be investigated more extensively. The nature of the residual solvent, as proposed by Storfer and Yuhas, may effect the slight tendency to blister that has been improved but still exists (7). Requests have been received, from the field, for white or grey versions of the traditionally black lining, in order to facilitate more efficient coverage in recoating operations. Laboratory work indicates that the use of a final, sealing topcoat can reduce acid and water penetration into the lining in immersion situations.

EXPERIMENTAL METHODS

An atlas cell test procedure was chosen for screening materials for corrosion resistance. The coating was applied to metal (usually carbon steel) according to the application method being evaluated. The cell was approximately one-half filled with a mixture of 5% sulfuric and 0.5% hydrochloric acid, aerated using an aquarium pump and heated to the test temperature (usually to 150°F). The cells were disassembled and the panels examined on a monthly schedule. When failure occurred, the usual mode of failure was through the formation of small blisters. This sometimes occurred in the vapor contact area and sometimes in the liquid contact area. The region of failure was fairly consistent for a given system. Once small blisters formed, rapid progression to blistering covering most of the contact area was usually observed within the next one to two months. Occasionally, a small blister was formed which did not signal rapid, progressive failure. This was judged to be due to a flaw in the coating due to poor application.

Thermal analysis (DSC) was performed on a Perkin Elmer instrument. Heating rates typically were $20^\circ\text{C}/\text{minute}$. Dry heat exposures were performed at temperatures up to 600°F in an indirect heated, forced air draft oven. Exposure times up to 6 months were used. Airless spray characteristics were

evaluated using equipment typical of field applications. Solvent release characteristics were evaluated by allowing samples to dry and cure for various times, placing them in the forced draft oven and heating to 400°F as rapidly as possible.

This occurred in 15-30 minutes with 20 minutes being typical. Samples were judged to fail if they developed any blistering or delamination under these conditions.

Tensile strength and elongation were run on an Instron Model 1122 in accordance with ASTM D412.

Adhesion was determined in accordance with ASTM D4541-85.

SUMMARY

A new, second generation, fluoroelastomeric coating was developed which is suitable for use in retrofit FGD systems. The incentive driving the development of the new generation was the poor performance of the first generation coating. Field performance of both generations of linings is discussed and mechanisms for the failures are proposed and briefly discussed. This paper presents laboratory testing results and relates them to field performance. Finally, a program for the development of a third generation coating is outlined.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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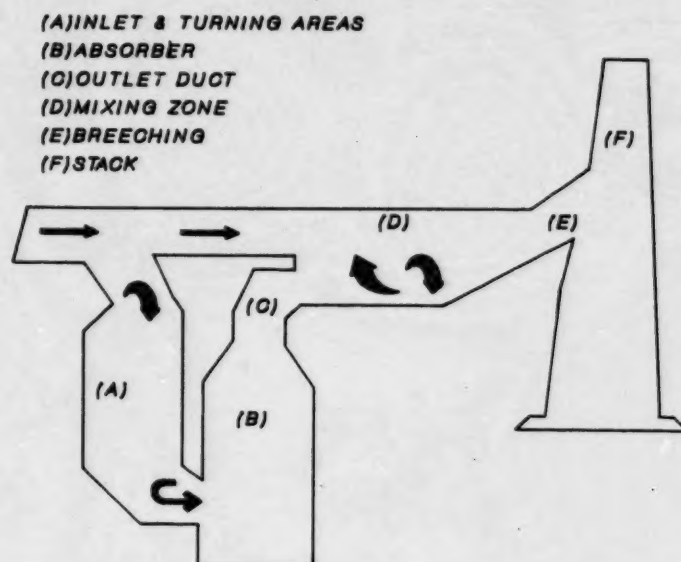


Figure 1. Typical wet FGD system.

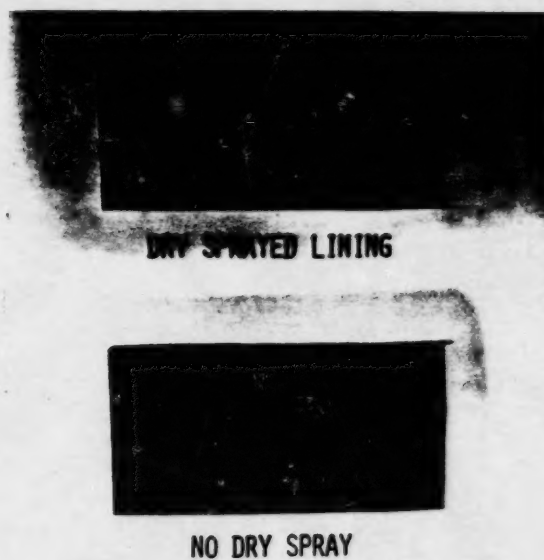


Figure 2. MEK borne lining (top), Second generation lining (bottom)

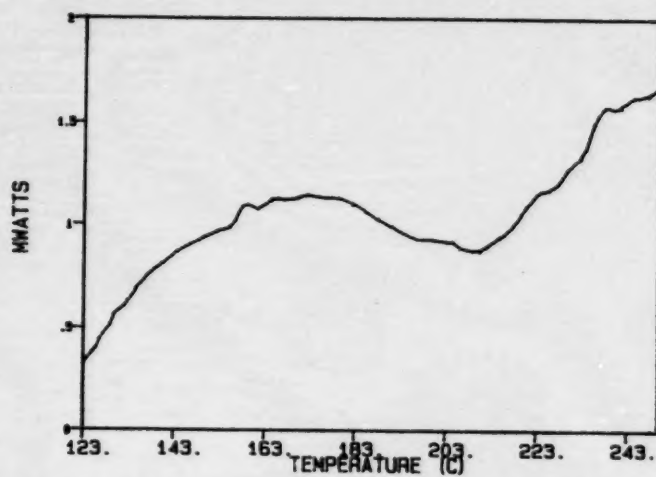


Figure 3. DSC curve of first generation fluoroelastomer.

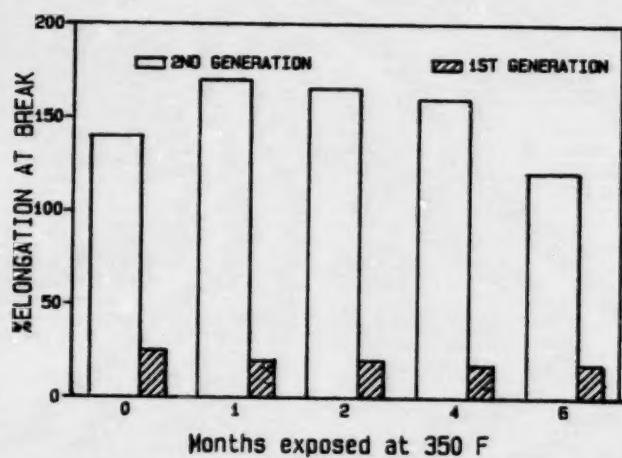


Figure 4. % Elongation at break after dry thermal exposure of free films.

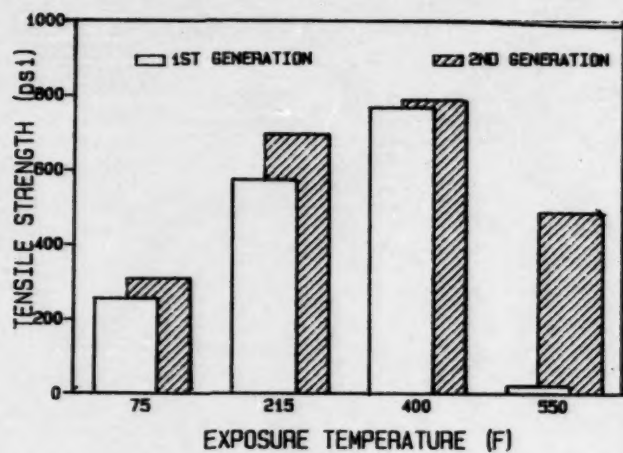


Figure 5. Change in Tensile Strength (psi), of free films, with dry thermal exposure.

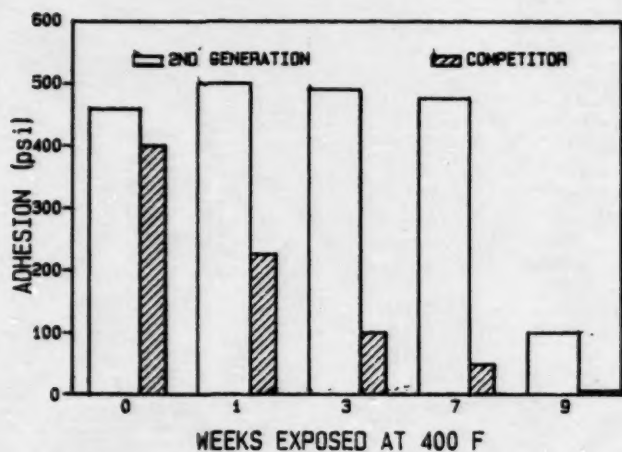


Figure 6. Change in Elcometer adhesion (psi) with dry thermal exposure at 400°F.

TABLE 1. FLUOROELASTOMER ADHESION WITH DRY THERMAL EXPOSURE

<u>Blast Profile (mils)</u>	<u>Film Thickness (mils)</u>	<u>Elcometer Adhesion (lb/in²)</u>	
		<u>138 days @ 350°F</u>	<u>170 days @ 350°F</u>
2-3	20-25	435	460
2-3	35-40	<50	<50
4-5	20-25	425	485
4-5	35-40	400	450

TABLE 2. PROPERTIES OF FLUOROELASTOMER LINING MATERIALS

	<u>First Generation</u>	<u>Second Generation</u>
Film thickness per coat (microns)	125	125-200
Potlife (hours)	1	>8
Recoat time (at 75°F) (hours)	16-24	6-8
Final dry time at 75°F (days)	7	4-5
Start-up schedule	yes	none
Can stability	hard settle	no settling

LIFE-CYCLE COST MODEL FOR FGD COMPONENTS*

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ABSTRACT

The use of stainless steels and nickel-based alloys in the utility industry is increasing rapidly in the United States and overseas. Utilities use these materials in flue gas desulfurization (FGD) systems to minimize corrosion-related failures. Stainless steels and nickel-based corrosion-resistant alloys are preferred materials for both new and retrofit applications. A life-cycle cost model was designed for use on IBM and compatible personal computers to facilitate the selection of construction materials by the analysis of "what-if" scenarios during project planning. A life-cycle cost comparison of materials alternatives is essential in the selection of the materials of construction.

The cost model generates a summary table that permits the comparison of life-cycle costs of major FGD components under nine different user-selected scenarios. Model input consists of cost and construction configuration parameters. Each scenario covers three sizes of three different FGD components.

Work is currently underway to extend this computer model to include sheet lining or "wallpapering" as one of the construction options. Recent field experience using sheet lining with high-alloy nickel-base corrosion-resistant materials such as Alloy C-276 indicate that still further cost savings are possible with this construction technique.

* The work described in this paper was not funded by the U.S. Environmental Protection Agency; therefore, the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

LIFE-CYCLE COST MODEL FOR FGD COMPONENTS

METHODOLOGY

Life-cycle costs take into account all the relevant costs of a system over its lifetime. For a meaningful comparison of available options, life-cycle costs must be all-inclusive, i.e., they must include all the direct and indirect costs. The following cost components were analyzed for a life-cycle cost comparison of FGD system materials of construction:

- ° Initial capital investment
- ° Major maintenance
- ° Routine maintenance
- ° Insurance and miscellaneous annual charges
- ° Depreciation tax credit

All of the above cost components are affected by the material of construction. The operating costs (i.e., the costs of raw materials, utilities, and operating and supervisory labor) are assumed to be independent of the materials of construction and thus are not included in the analysis.^{1,2}

The Electric Power Research Institute (EPRI) has published guidelines for performing cost analyses of utility projects in a report entitled "Technical Assessment Guide" (TAG).³ These guidelines provide a consistent set of economic factors, financial assumptions, and other cost-estimating parameters necessary for utility projects.

CAPABILITIES AND FEATURES

The life-cycle cost model allows the user to calculate the life-cycle costs of the FGD scrubber/presaturator, absorber, and outlet ductwork. The model will calculate the costs of three sizes of each component for the comparison of selected material configurations. The gas-flow rates of the selected sizes are 285,000, 427,000, and 570,000 acfm, which are equivalent to about 100, 150, and 200 megawatts of electrical capacity, respectively.

The model allows the user to generate country site-specific life-cycle costs. The user can select any one of 13 countries for the run. To obtain a site-specific run, the user merely selects the appropriate input information. The countries included in the model are:

Australia
Belgium
Canada
Denmark
Federal Republic of Germany
France
Italy

Japan
Netherlands
Norway
Sweden
United Kingdom
United States of America

Various high-alloy materials have been tried and found to be successful for use in FGD equipment. Based on a literature review and the FGD data base maintained by PEI, 12 materials were selected for the model as default materials. These materials are grouped under three categories; the categories and materials under each category are:

° Stainless Steels

Type 316L
Type 317LM
Alloy 904L
Duplex Alloy^{*}255
Alloy 254SMO

° Low-Molybdenum Nickel-Base Alloys

Alloy 825
Alloy 20Cb-3^{**}
Alloy G
Alloy 20Mo-6^{**}

° High-Molybdenum Nickel-Base Alloys

Alloy 625
Alloy C-276
Alloy C-22

The compositions of the corrosion-resistant alloys selected for this analysis are summarized in Table 1.

The user can also select up to 12 construction materials for each component and can specify alloy-clad construction or the solid construction option for each material and component. Although the model presents costs for the built-in construction material as default values, the user can select alternative materials and can also alter the material costs. The model permits the user to run single or multiple configurations.

The program will support various levels of input. The model has default values for input parameters to aid the user. The user can selectively change this default information or can provide a completely new set of parameters.

^{*} Trademark of Avesta AB.

^{**} Trademark of Carpenter Technology Corporation.

PROGRAM STRUCTURE

The life-cycle cost program runs in an interactive mode to give the user total control over the program input and to allow the analysis of "what-if" scenarios. The program generates prompts for entering input data and verifies the data upon entry.

Figure 1 is a flow diagram of the cost model. The model includes a "read-only" parameters file containing default data that can only be changed externally. It also includes an active default parameter file that allows the user to save the values used in the current run for future use. Before leaving the program, the user can save the current data. If the current data are not saved, the contents of the active file are replaced with the permanent defaults from the "read-only" file.

The program permits the user to generate life-cycle costs for multiple configurations in a single run and displays the results in a table. The user can also generate a printed report that can include input data and results or results only.

EXAMPLE OF MODEL APPROACH

The task is to develop a life-cycle cost comparison for the following FGD construction scenario:

- Country--United Kingdom
- Gas flow rate unit = m^3/hr
- Conversion factor for gas flow = 1.7
- Scrubber/presaturator
 - 50% 904L solid construction
 - 50% Alloy C-276 clad construction
- Absorber
 - 25% Type 316L solid construction
 - 25% Type 317LM solid construction
 - 30% Alloy 904L solid construction
 - 20% Alloy C-276 clad construction
- Ductwork
 - 100% Alloy C-276 clad construction
- System life = 40 years
- Liner replacement frequency = 5 yrs
- Material prices
 - Lined-carbon steel = £ 3,500/tonne
 - Type 316L = £ 2,700/tonne
 - Type 317LM = £ 3,250/tonne
 - Alloy 904L = £ 5,000/tonne
 - Alloy C-276 = £ 15,000/tonne
- Maintenance factors = 12% for lined-carbon steel, 1% for Alloy C-276, and 2% for other materials
- Taxes and insurance = 2%
- Construction labor rate = £ 22.00/hr
- Discount factor = 6%
- Income tax basis = 35%
- Depreciation schedule = 5% for every 5 years beginning with 5th year

Step 1

Using the built-in labor and material quantities for the nine cases (three components--scrubber, absorber, and ductwork--and three sizes--small, medium, and large) and user-supplied carbon steel plate and construction labor rates, the program calculates the labor and material values for baseline cases. The labor and material values for each case are then combined to obtain the baseline component costs.

Step 2

The user provides material prices for the selected materials. Carbon steel plate and construction labor costs are the default values or are modified by the user.

Step 3

The presaturator/scrubber is to be constructed of Alloy 904L and Alloy C-276 materials. It is 50 percent solid and 50 percent clad construction. The cost of solid construction options are calculated using the default or user-supplied material costs. The cost of clad construction is calculated assuming that the cost equals half of the solid alloy construction option. Labor costs are added to obtain the costs of the solid alloy and clad construction options. The final cost is calculated by using 50 percent of the solid alloy cost and 50 percent of the clad alloy cost.

Step 4

The program calculates the installation labor cost for each size of the scrubber by multiplying the baseline labor cost by the built-in labor factor.

Step 5

The material and labor values for each scrubber size are combined to obtain the installed cost of the scrubbers.

Step 6

The absorber in this example is to be constructed from four materials (carbon steel is used as the substrate for all clad options). The costs of the alloy-clad construction option in the model are based on the assumption that they equal half of the solid alloy construction option. This applies to both carbon steel and alloy. The material costs for each individual material option is calculated by using the appropriate material rate and then multiplying by 0.5 (for clad construction). The labor costs, which are assumed to be 10 percent higher for alloy-clad construction, are calculated for individual material options by multiplying the baseline labor costs in Step 1 by 1.1. For each construction material, the labor and material costs of each of the three sizes are added together to obtain the installed costs of the absorber.

Step 7

For each absorber size, the installed cost of the selected material combination is calculated by multiplying the installed cost of the individual materials (calculated in Step 6) by the material percentage specified by the user.

Step 8

The installed cost of each of the three outlet ductwork sizes is calculated by a procedure similar to that for the scrubber/presaturator in Steps 3, 4, and 5. The material cost for each size of the ductwork is multiplied by 0.5 to account for the alloy-clad construction.

Step 9

The initial capital cost of each component is calculated by multiplying the installed cost by direct and indirect cost factors provided by the user. The annual cash flows, such as maintenance, taxes, insurance, and depreciation tax credit, are calculated as a percentage of capital cost and distributed over the duration indicated by the user. The program also enables the user to include additional cash flows (other costs and credits). The user provides these data as a percentage of capital cost by year over the lifetime of the system.

Step 10

The life-cycle cost of each option is calculated by combining the cash flows by year over the life of the system and discounting them to the current year by applying a user-selected discount factor. The life-cycle cost is then divided by the gas flow rate for each size to obtain the life-cycle cost on a per-unit basis.

DATA LOADING

The user provides the data needed for the program in an interactive mode by using nine input screens. The program also contains default data files to assist the user in data loading. The data input screens are described below.

Final Report Parameter

The final report parameter screen allows the user to load user name and report title for the printed report.

Country-Specific Parameters

This screen allows the user to select the country (from the 13 available) and corresponding currency. The screen also allows the selection of the unit to be used for gas flow rate.

Configuration Name

The program can analyze multiple configurations in a single run. The configuration name screen allows the user to load the configuration identification information.

Configuration Data

The configuration data screen allows the user to load percentages for construction materials and the construction type (alloy-clad or solid alloy) for each of the three FGD components. The user can select any combination of construction materials and construction type for each component; however, the total percentage for each component must equal 100. The users can also introduce new construction materials by typing their names over the unused materials in the table.

Material Prices

For the materials indicated on the configuration data screen, material prices are needed to estimate the capital cost of the FGD components. The material prices screen allows the user to select the material prices and the percentages for routine maintenance. The routine maintenance percentages are expressed as a percentage of the capital cost of the baseline option.

Cost and System Parameters

This screen allows the user to load the data required to extend the installed costs to capital costs and the data required to make present-worth calculations.

Depreciation Schedule

This screen provides the depreciation life, depreciation percentages, and the income tax basis for calculating depreciation tax credits. When the depreciation life has been indicated, the screen presents a table for loading depreciation percentages over the indicated life. The capital cost is multiplied by the depreciation percentage and income tax basis, and the resulting value is included as a credit in the present-worth calculations.

Schedule of Other Variable Costs

This screen, which is similar to the depreciation schedule screen, permits the loading of user-defined annual costs as a percentage of capital cost. The user first indicates the number of years over which these costs are to be incurred, and the screen then presents a table on which the user can load percentage by year.

Schedule of Other Variable Credits

This screen is similar to the schedule of other variable costs except that the values derived from the screen are included as credits. Table 1 defines the input variables for the cost model and indicates the default for each of these variables.

LIFE-CYCLE COST MODEL EXECUTION

The program output consists of a set of nine life-cycle cost values for each configuration selected by the user. The costs are presented in the currency and gas-flow units specified by the user. The results are displayed on the computer screen in a table format. The user can also print a report of the results and input data.

The program is designed to run on IBM or compatible personal computers. The user is provided with a magnetic disk containing the compiled binary code of the program. The user can customize the program by "read-only" defaults prior to routine use.

CUSTOMIZATION

The program-customization feature allows the user to load user-specific default data in the "read-only" file. A customized version will facilitate the routine use of the program by presenting the user-preferred default data each time the

program is accessed. To customize the program, the user follows exactly the same data input procedure as used for running the program. At the end of the customizing routine, however, the input data are stored in the "read-only" file (for use during normal running of the program) and the user is returned to the operating system. The data loaded during the customization phase are available as default data for all program operations until the program is recustomized.

The user accesses the customizing routine by 1) selecting the directory where the life-cycle cost program is located, and 2) by typing (from the operating system) "FGD CSTMZ" and pressing the "Enter" key. Appropriate sections of the manual provide input definitions and data loading procedures.

PROGRAM OPERATING MODES

The program can be run in a normal mode or a "quick-run" mode. The quick-run mode bypasses introductory screens and takes the user directly to the data-loading screens. The normal mode shows the title and introduction screens. To run the program in a normal mode, the user must 1) select the directory under which the life-cycle cost program is stored; and 2) from the operating system, type "FGD" and press the "Enter" key. To run the program in a quick-run mode, the user must type "FGD QRUN" instead of "FGD" in Step 2.

Normal keyboard entry conventions are used to load the data. The program has built-in error-trapping and data-verifying routines that display appropriate messages to guide the user.

LIFE-CYCLE COST MODEL APPLICATION

Stainless steels and other corrosion-resistant alloys are finding wider application in utility FGD systems; these materials are increasingly being used in new installations and are also replacing conventional organic linings in existing applications. Depending on the nature of application, the FGD operator can select from a wide variety of stainless steel and high-alloy material grades. The best combination of construction materials and individual components is selected to determine optimum material use. The material and construction type can also be varied within each component depending upon the operating environment. The life-cycle cost model allows the user to compare life-cycle costs of various materials and construction configurations that are actually used.

Although capital costs of FGD components constructed of stainless steel and other corrosion-resistant alloys are generally higher than those of conventional lined-carbon steel components, the life-cycle costs are usually substantially less. Figure 2 shows a life-cycle cost comparison for the following material selection scenario:

- ° Solid-alloy scrubber/presaturator
- ° Alloy-clad carbon steel absorber
- ° Alloy-clad carbon steel ductwork

Figure 2 is based on the assumption that a single material is used for all three FGD components and the construction configuration cannot be varied for individual components. This constraint does not allow the optimization of construction materials. Figure 2 shows that even under less than optimum material use scenarios, however, the life-cycle costs of stainless steels and other corrosion-resistant materials are significantly lower than the neoprene-lined carbon steel

option with the exception of high-molybdenum nickel-base alloys. The costs in Figure 2 are based on guidelines published by the Electric Power Research Institute for performing cost analyses of utility projects in the United States. These guidelines provide a consistent set of economic factors, financial assumptions, and other cost-estimating parameters for utility projects.

The life-cycle cost model allows the user to refine the analysis such as the one in Figure 2 by affording the flexibility to vary the material and construction type within each component and among the individual components. Use of the best material will result in life-cycle costs that are lower than the costs of lined-carbon steel systems. The life-cycle cost model allows the user to analyze material use scenarios that represent actual construction configurations. Table 3 shows a cost comparison for the example discussed in this paper under the subsection Program Structure. A cost comparison of components with multiple materials and multiple construction options cannot be easily performed without the life-cycle cost model.

The life-cycle cost analysis understates the cost savings associated with corrosion-resistant alloys. These alloys are resistant to catastrophic failures associated with excursions in operations (e.g., plugging of a line resulting in overheating or lack of neutralization). The cost comparison also does not account for the downtime or shutdowns attributable to material failure. Even a small improvement in this area can result in large cost savings. The use of more corrosion-resistant materials such as stainless steels and nickel-base alloys can greatly reduce the system downtime and shutdowns attributable to material failures.

TECHNICAL SPECIFICATIONS

The technical specifications for this model are as follows:

- ° System Requirements--IBM personal (or compatible) computers with 80-column printer
- ° Memory required--128 k
- ° Display modes--This program will run either on a monochrome or color monitor. It adjusts itself to the available monitor.
- ° Programming language--This program's source code is written in "C" and assembly language. Portions of the program were compiled with the Microsoft C compiler Version 3.0 (copyrighted by Microsoft Corporation, 1984, 1985) and assembled with the Microsoft Macro Assembler Version 4.0 (copyrighted by Microsoft Corporation 1981, 1982, 1983, 1984, 1985).

SUMMARY

Nickel alloys and stainless steels are being specified or considered for application in FGD equipment where advantage can be taken of their durability, long life, and low maintenance. This well established trend may become worldwide as the cost-effectiveness of the use of appropriate nickel materials is acknowledged.

By careful design and application of fabrication techniques to take full advantage of the properties and characteristics of nickel alloys and stainless steels, the lowest cost components and equipment can be developed.

The life-cycle costing approach permits a ready evaluation of the effects of modifications of material selection, of the form in which the material is utilized, and the proportions of materials used in different parts of the FGD system.

With the knowledge of the service conditions of temperature, pH, chloride ion concentration, etc., material selection may be optimized. The use of a higher grade but more expensive alternative may be suggested, however, to compensate for extreme or over-load conditions to minimize potential increases in maintenance costs. The effect of such an upgrading can readily be compared using the model.

The model indicates that life-cycle costs of FGD components constructed of nickel-containing steels and alloys are often substantially less than those of nonmetallic lined-carbon steel structures, although the capital costs are frequently higher. The life-cycle model permits a ready comparison of the benefits, coupled with wide flexibility in use with the multiple choice of material, fabrication, and proportions options open to the user in readily accessible form on the PC.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the Nickel Development Institute that made this study possible.

AVAILABILITY OF PROGRAM

The User's Manual and the program disk may be obtained at no charge by contacting the Nickel Development Institute or one of the authors.

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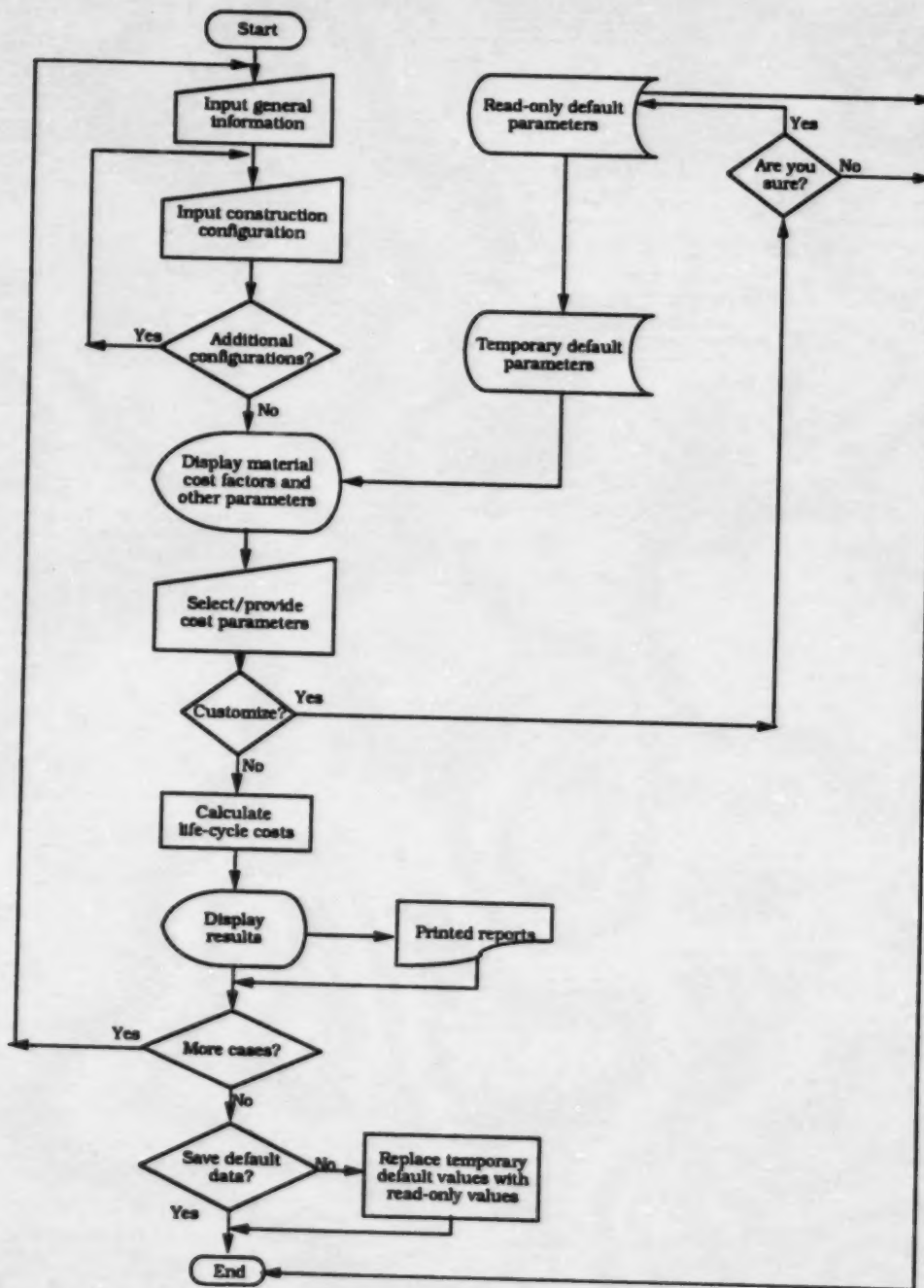


Figure 1. Flow Diagram

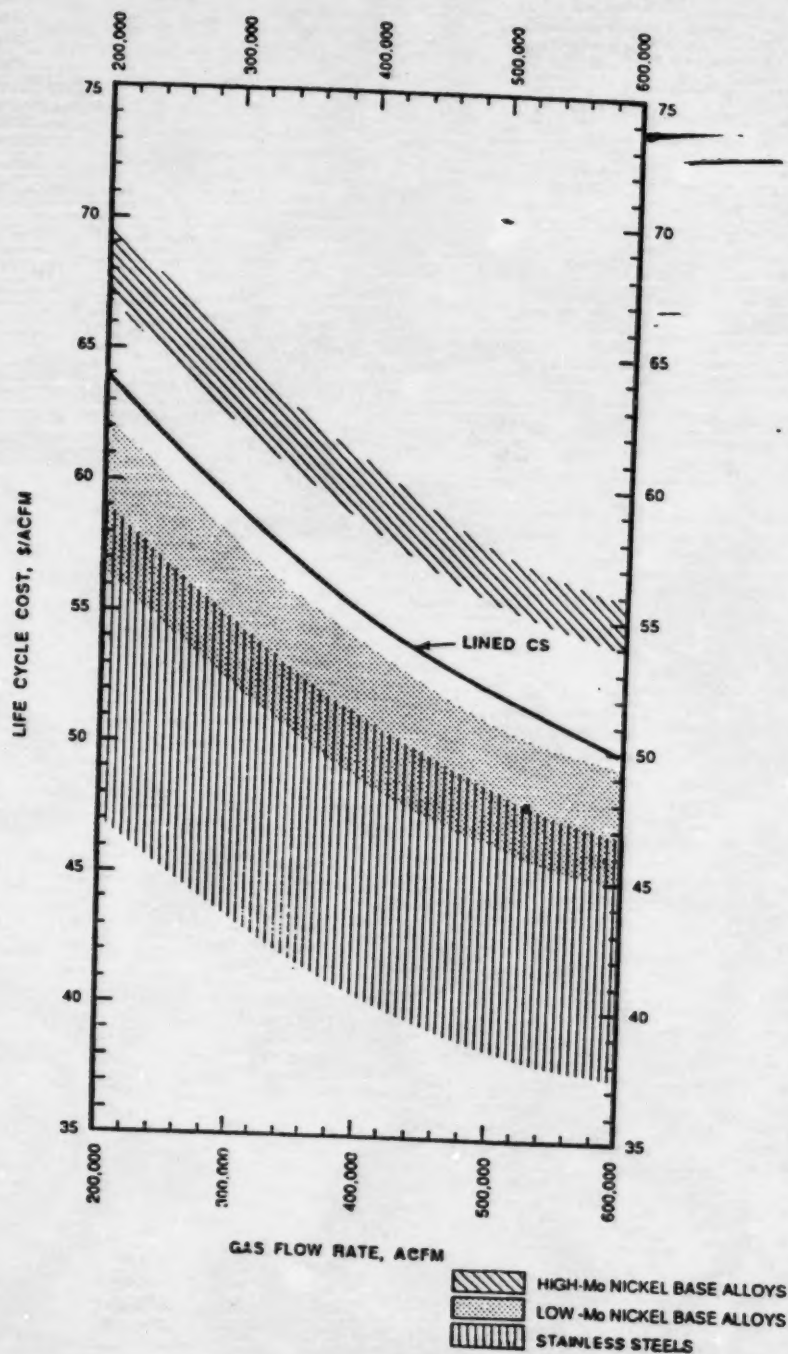


Figure 2. Life-cycle cost comparison, combined system.
(1000 acfm = 0.472 m³/s).

TABLE 1. COMPOSITIONS OF CORROSION RESISTANT MATERIALS

UNS ^a No.	Alloy	Nominal composition, weight percent								
		Ni	Mo	Cr	Fe	Cu	W	Cb	N	C, max. %
S31613	S.S. 316L	10	2	16	70	-	-	-	0.05	0.030
S31725	S.S. 317LM	15.5	4	18.5	62	-	-	-	0.06	0.02
N06625	Alloy 625	61	9	22	3	-	-	4	-	0.10
N08825	Alloy 825	42	3	22	30	2	-	-	-	0.05
N08904	Alloy 904L	25	5	21	45	2	-	-	-	0.020
N06007	Alloy G	44	7	22	20	2	1	2	-	0.05
N10276	Alloy C-276	56	16	16	5	-	3.5	-	-	0.010
S31254	Alloy 254SMO	18	6.1	20	Bal.	0.7	-	-	0.2	0.020
S32550	Duplex Alloy 255	6	3	25.5	Bal.	2	-	-	0.2	0.04
N08026	Alloy 20Mo-6	34	6	23	Bal.	3	-	-	0.10	0.03
N08020	Alloy 20Cb-3	34	2	20	Bal.	3.5	-	0.5	-	0.07
N06022	Alloy C-22	Bal.	13	22	3	-	3	-	-	0.010

^a UNS = Unified Numbering System.

TABLE 2. INPUT PARAMETERS

Input variable	Description	Default value
User name	A character string used in the printed report heading. May be any string of 50 characters or less.	"User name"
Report title title"	A character string used in the final report title. May be any string of 20 characters or less.	"Report"
Country and currency	The country and currency for the run	U.S.A..\$
Unit for gas flow rate	Unit for gas flow rate	acfm @300° F
Specify 'Other'	A user preferred unit for gas flow rate (used only when "other" gas flow unit is selected).	None
Gas flow rate conversion factor	A numerical value for converting gas rate to 1 acfm(used only when "other" is selected)	0
Configuration ID	Configuration identification number or name	1
Material name	A character string used to identify construction material	material specific
Construction configuration percentages	Material and construction configuration percentages for each component	0
Material prices	The prices of materials selected by the user for the run.	material specific
Routine maintenance factor	Annual routine maintenance factor for the selected materials relative to the capital cost of the lined carbon steel	material specific
System life	Useful life of the FGD system (Max., 60 years).	30

(continued)

Table 2. (continued)

Input variable	Description	Default value
Direct cost factor	Multiplier for direct cost	1.5
Indirect cost factor	Multiplier for indirect costs, such as engineering freight, contingencies, etc.	1.76
Liner replacement frequency	Estimated liner replacement frequency for the baseline system	5
Annual taxes and insurance	Percentage of the capital cost that will be incurred as annual tax and insurance cost.	2.0
Construction labor rate	Construction labor rate in the country selected.	\$11.48
Discount factor	Discount factor used for present-worth calculations. Expressed in constant dollars.	6.1
Depreciation lifetime	The number of years over which FGD components are to be depreciated.	5
Depreciation basis	Depreciation as percentage of capital cost by year.	20
Income tax basis	Income tax rate that will be applied to depreciation.	38
Lifetime of variable costs	Number of years for other cash flow expenditures.	5
Schedule of other variable costs	The percentage of capital cost for user-defined cash-flow expenditures.	0
Lifetime of variable credits	Number of years for user-defined credits associated with FGD system	5
Schedule of other variable credits	Percentage of capital cost for user-defined credits by year.	0

TABLE 3. LIFE-CYCLE COST COMPARISON FOR EXAMPLE CASE
(£/cu. m./hr)

Configuration	Scrubber/presaturator		Absorber		Ductwork		Total cost	
	small	medium	small	large	small	medium	small	large
Lined-carbon steel	68.67	62.58	80.45	75.16	71.73	47.61	203.27	185.35
Example case	73.56	67.03	64.15	59.93	57.20	66.76	213.65	193.72
								174.55
								181.99

PERFORMANCE OF LININGS IN FGD SYSTEMS

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ABSTRACT

As part of a study for EPRI, Battelle analyzed the field performance of various types of protective linings in different components of FGD systems. The linings included acid-resistant brick and mortar in prescrubber sumps at San Juan, natural rubber in absorbers at Somerset, chemically bonded concrete over a mica flake-filled polyester membrane in outlet plenums at Four Corners, glass flake-filled polyester in breechings at Petersburg, and fluoropolymer in flues at Bruce Mansfield.

Field visits were made to each site to obtain background information, inspect the lining, and collect samples for detailed analysis. Appropriate types and methods of analysis were selected for each specific case. The results were used to evaluate performance and/or determine causes of failure. The performance ranged from complete failure of the glass flake/polyester lining because of temperature excursions to relative success with the fluoropolymer lining exposed only to saturated, scrubbed flue gas. The performance of a lining depends upon materials specifications, application procedures, and exposure environment.

INTRODUCTION

About 150 flue gas desulfurization (FGD) systems are currently in operation on coal-fired utility boilers in the U.S. Wet scrubbing processes account for 92 percent of the total controlled capacity of about 65,000 MW. Corrosion and degradation of materials of construction continue to be major problems in maintaining wet FGD systems.

Field surveys of the performance of materials in FGD systems have served to classify the various system components into three categories: 1) low history of materials problems and/or amenable to rapid repair or replacement, 2) moderate history of materials problems and/or difficult to repair or replace, and 3) significant history of materials problems and/or failures result in loss of generating capacity for long periods of time (1, 2). Prescrubbers and absorbers are among the components in the second category,

while outlet ducts and stack linings comprise the components in the third category. Under sponsorship of the Electric Power Research Institute (EPRI), Battelle is conducting a systematic investigation of the causes of materials failures in FGD system components.

Most FGD system components are fabricated from carbon steel or corrosion-resistant alloys. Usually, carbon steel must be lined to protect against corrosion. Both organic and inorganic lining systems are used, depending upon the environment. As part of the study for EPRI, Battelle has assessed the performance of linings in various FGD system components. This paper presents results of performance assessments of five different types of linings on five different components at five wet FGD installations on utility boilers.

BACKGROUND

In order to assess the performance of linings, it is necessary to know the environmental conditions to which the linings are exposed as well as the properties of the linings.

SERVICE CONDITIONS

The various FGD system components are exposed to different service conditions. These conditions are defined by the temperature, chemistry, and abrasiveness of the environment. As shown in Table 1, the ASTM has identified three levels of severity, from 1 (mild) to 3 (severe), for classifying each environmental factor (3). For example, the mildest condition encountered can be coded 1-1-1 and represents a temperature below 140°F (60°C) a pH of 3 to 8 with low concentrations of chloride and fluoride, and low velocity fluid flow. By contrast, the most severe condition can be coded 3-3-3 and represents a temperature above 200°F (93°C), an acid concentration greater than 15 percent with high concentrations of chloride and fluoride, and high energy fluids with entrained particulates.

Service conditions can vary in different regions of a given component. The inlet of a venturi prescrubber can be exposed to the most severe environmental condition (3-3-3), while the sump is exposed to a mild temperature and an intermediate acidity and abrasiveness (1-2-2). Except for the wet/dry zone (if there is no prescrubber) and areas of direct spray impingement, the service conditions in an absorber are mild. Outlet ducts and stack linings (flues) are subjected to a variety of service conditions depending upon the configurations of the ductwork. The various configurations and service conditions are outlined in Table 2. The mildest operating conditions (1-1-1) are encountered when there is no reheat and no bypass. More severe conditions are encountered under full or partial bypass operation (3-0-2 and 2-2-2, respectively). The mixing zone for wet scrubbed gas and hot bypassed gas is exposed to an aggressive environment due to condensation of acidic species (SO_3 , HCl , and HF) from the bypassed gas and to temperature variations within a very small area.

TYPES OF LININGS

Organic lining systems can be divided into two types -- resin and elastomer. Organic resin linings have been used extensively in prescrubbers, absorbers, outlet ducts, stacks, and tanks. The service environment generally limits the types of resins that can be used to polyester, vinyl ester, and epoxy. Even these resins are limited to a maximum temperature ranging from 180°F (82°C) under wet conditions to 360°F (182°C) under dry conditions,

depending upon resin type. Organic resin linings usually contain fillers to decrease permeability and increase strength. These linings are applied in liquid form by spray, roller, or trowel. Failures can be caused by improper application, temperature excursions, permeation by acidic liquids, and/or wear from abrasive fluids.

Organic elastomer linings have been used in the same components as the resin linings. Elastomer linings include natural or synthetic rubber applied in sheet form, and fluoropolymers applied in liquid form as a spray. Rubber has a temperature limitation of about 180°F (82°C). Fluoropolymers can withstand temperatures up to 400°F (204°C). Elastomer linings can also fail due to improper application, temperature excursions, and permeation by acidic liquids, but are more abrasion resistant. Rubber is flammable so that care must be taken to prevent fires.

Nonmetallic inorganic lining systems can also be divided into two types -- cementitious monolithics and prefired shapes and mortar. Cementitious monolithics have been used in prescrubbers and outlet ducts. They include calcium aluminate cement-bonded concretes that harden by hydration, and potassium silicate-bonded concretes that harden by chemical reaction using a silicofluoride, phosphate, or organic hardening agent. Both types of concrete linings are usually applied with a pneumatic gun (gunite technique), but they can also be cast or troweled. For FGD service conditions, these linings are applied over a wire mesh for reinforcement. The cement bonded concretes can withstand temperatures of 500°F (260°C), but are attacked by a dissolution mechanism in sulfuric acid when the pH is below 4. Silicate bonded concretes are more temperature and acid resistant, but are subject to cracking and permeation by acidic liquids. Organic resin linings have been used as a membrane under the concrete to protect the steel substrate from corrosion by the permeated liquid.

Prefired shapes include foamed, closed-cell borosilicate glass blocks and acid-resistant bricks (red shale and fireclay). Glass blocks have been used in outlet ducts and acid-resistant bricks in stack liners. These materials can withstand high temperatures and are resistant to chemical attack. Glass blocks are bonded together with a urethane/asphalt mortar, while bricks are joined with a silicate bonded mortar that is similar to the chemically bonded concretes. Brick linings in stacks are typically free standing flues rather than a protective lining for a steel substrate. Acid-resistant bricks have also been used to line prescrubber sumps in some regenerable FGD systems. In these cases, the mortar is carbon-filled furan. Glass blocks are prone to mechanical damage and can be difficult to clean because deposits tend to be very adherent. In some cases, glass blocks on a duct floor have been covered with a gunite lining to provide protection from mechanical damage. Brick and mortar are both prone to penetration by acidic liquids and to moisture expansion. Differential moisture expansion has been identified as the cause of leaning brick flues (4).

ASSESSMENTS OF LININGS PERFORMANCE

The field performance of five different types of linings on different components of five FGD systems was assessed by Battelle with funding provided by EPRI. The linings included acid-resistant brick and mortar in the prescrubber sumps at San Juan, natural rubber in the absorbers at Somerset, a chemically bonded concrete over a mica flake-filled polyester membrane in the

outlet plenums at Four Corners Units 4 and 5, a glass flake-filled polyester in the stack breeching at Petersburg Unit 3, and a fluoropolymer in the flues at Bruce Mansfield Units 1 and 2. A team of specialists visited each site, usually during a boiler shutdown. The purpose of the visit was to (1) interview plant personnel to obtain background information, operating history, and service conditions for the lining; (2) inspect the linings whenever possible; and (3) obtain samples of the linings and scrubbing liquors or condensates for detailed analyses. The results of these analyses were used to evaluate the performance of the linings.

ACID-RESISTANT BRICK AND MORTAR LINING IN PRESCRUBBER SUMPS AT SAN JUAN

The San Juan Power Plant of Public Service Company of New Mexico has four generating units fired with 0.8 percent sulfur coal. The units are equipped with Wellman-Lord FGD systems. Each unit has four FGD modules consisting of venturi prescrubbers and tray tower absorbers. The towers are made of steel-reinforced concrete lined with ceramic tile. The bottom portion of each tower, which serves as the sump for the prescrubber, has a mastic membrane over the tile. The membrane is covered with a single layer of acid-resistant fireclay bricks bonded with a carbon-filled furan mortar. The interior faces of the sump walls have a 3-1/2 to 4 in. concave camber in the horizontal direction to provide an arc contour for brick compression. There are no expansion joints in the tile or brick linings.

In the prescrubbers, the flue gas is quenched with river water to remove fluorides, chlorides, SO_3 , and residual fly ash from hot electrostatic precipitators. Flue gas and scrubbing liquor from a venturi enter an absorber vessel through a circular duct on the east wall at about the center of the sump. The liquor collects in the sump and the flue gas turns upward and passes through a mist eliminator and a chimney tray before entering the absorber section of the tower. A bleed stream from the sump is neutralized with lime and sent to a settling pond.

After about two years of operation, the bricks in some of the sumps exhibited surface corrosion, and about half of the prescrubber sump walls in Units 3 and 4 bulged inward (refer to Figure 1). About half of the major bulges are in west walls. In one module, the east and west walls bulged so badly that all four walls had to be torn down and replaced. Brick samples from the west wall of this module, as well as unexposed brick samples and a sample of sump liquor, were obtained for analysis. Chemical analysis of the bricks indicated a leaching of aluminum, potassium, and iron from the exposed surface. This surface was found to be enriched in fluorine and sulfur, suggesting that one or both of these species may be contributing to brick corrosion. Chemical analysis of the sump liquor indicated a pH less than 2, a fluorine concentration greater than 400 ppm, and a fluorine/aluminum mole ratio of about 10. This mole ratio suggests that free fluoride (fluoride ions uncomplexed by aluminum ions) is present. The brick surface corrosion is most likely due to fluoride attack. However, it is not a major problem because the attack has not penetrated beyond a depth of 0.1 in.

The bulging wall is a much more serious problem, but the primary cause is difficult to pin down. Moisture expansion commonly occurs in siliceous bricks exposed to a moist environment (4). The expansion is irreversible in the field, but can be recovered and, thus, measured in the laboratory by heating the brick to 930°F (500°C). A brick sample from the area of the bulge was found to have an average moisture expansion of 0.065 percent. The thermal

expansion for the same brick at the 125°F (52°C) service temperature in the sump is only 0.015 percent. Thus, the horizontal in-plane growth due to irreversible moisture expansion is about four times greater than that due to reversible thermal expansion. A detailed analysis is required to determine whether this growth can cause buckling of the cambered wall. However, simple geometric relationships show that a 0.065 percent increase in arc length for the 32 ft 2 in. long brick sump lining that is fixed at both ends would require an increase in camber from 4 in. to more than 7 in. Since the concrete wall behind the lining cannot be expected to move, and mortar shrinkage would not be expected to compensate for brick growth, it is reasonable to assume that the lining would bulge away from the wall.

In addition to horizontal growth, other possible causes of the lining bulges are vertical in-plane stresses and/or lateral loads. The vertical stresses can be due to the excess weight of a clogged mist eliminator and the lateral loads can be due to the solids or liquids that accumulate between the mastic and the tile as a result of penetration of the brick and mortar and/or seepage at the top ledge of the brick lining. However, the major bulges are predominantly in the west walls, while in all but one module, the mist eliminator beams are aligned so that the north and south walls provide continuous support and would be expected to have the highest stress concentrations. The west wall is directly opposite the flue gas entry duct and, thus, may be more prone to moisture expansion than the other walls.

NATURAL RUBBER LINING IN ABSORBERS AT SOMERSET

The Somerset Power Plant of New York State Electric & Gas Corporation consists of a single 643 MW generating unit fired with 2.5 to 3.0 percent sulfur coal. This unit is equipped with a wet limestone FGD system that includes six spray tower absorber modules in parallel, four for operation, one for maintenance, and one for standby. The absorbers have two 1/4 in. thick linings of natural rubber. The undermost lining failed as a result of attack by ozone during construction activities. This lining was overlayed with a second lining before the plant began full-scale operation. The second lining was cured in situ at ambient temperature and covered with a protective coating.

After about three years of operation, the outer rubber lining exhibited a nonuniform appearance. Some areas appeared to be in good condition, while other areas, both on the sidewalls and internal components, appeared to be swollen and had a puckered surface (refer to Figure 2). Also, the swollen areas may have debonded from the original lining.

A 50 in.² sample of the outer lining was supplied to Battelle for detailed analyses. Thermogravimetric analysis, extraction tests in acetone and toluene, and infrared (IR) analysis of the acetone extract provided data that made it possible to reconstruct the rubber formulation which is shown below:

<u>Component</u>	<u>Parts by Weight</u>
Natural rubber	100
Carbon black	45
Zinc oxide	5
Naphthenic process oil	2.5
Curing system	Not identified

Measurements of stress-strain properties (elastic modulus, tensile stress at the break point, and elongation at the break point) and hardness yielded results typical for a good quality rubber having the above formulation.

A cross-section of the lining was analyzed by scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). EDS, which cannot detect elements below atomic number 11, detected nine elements in the lining -- Si, S, Cl, Na, Al, Zn, Fe, Ca, and K -- listed in order of relative concentration. WDS was used to obtain concentration profiles for these nine elements plus fluorine. WDS detected five elements (Si, S, Cl, Zn, and K) in significant amounts. Zinc, Si, and some S are believed to be from the original rubber formulation, while Cl, K, and the remainder of the S are probably from the absorber liquor. The concentration profiles indicate that Cl and S, probably as SO_4^{2-} , diffused into the lining, the Cl all the way to the interface with the original lining and the S only near the outer surface. A reverse concentration profile that is difficult to explain was obtained for K. The concentration profiles for Si and Zn were flat.

In accordance with a recommended screening procedure (5), pieces of the rubber lining were immersed for 30 days in distilled water and various solutions to measure weight changes. The recommended maximum weight increase is 20 percent in distilled water at 180°F (82°C). The results, shown in Table 3, indicate that even an electric lineman's glove, which must have good water resistance to provide the necessary protection, does not meet this criterion. Furthermore, the weight change is highly dependent upon the composition of the immersion liquid and the immersion temperature. Immersion in 5 percent H_2SO_4 , another suggested test (5), produced a drastically lower weight increase than immersion in dilute acid or distilled water. Immersion in Somerset absorber liquor at 125°F, which simulates the environment inside the absorber, resulted in less than one-third of the weight increase obtained in distilled water at the same temperature.

In an attempt to determine why the rubber lining is much more resistant to swelling in absorber liquor than in distilled water, the 30 day immersion test was performed in various solutions of individual salts. The salts and solution concentrations were based on a chemical analysis of the soluble portion of the absorber liquor. This analysis is shown below:

<u>Species</u>	<u>Concentration (ppm)</u>
Cl	7950
Ca	2640
SO_4	2270
Mg	1160
Na	559
B	200
F	15 (estimate)
K	12

The immersion test results (refer to Table 3) indicate that magnesium may be the chemical species in the absorber liquor that is responsible for reducing the swelling of the rubber. Additional immersion tests in mixed salt solutions are required to confirm this hypothesis.

The most probable cause of premature failure of the rubber lining is inadequate resistance to the fluids present in the absorber. The lining is

very sensitive to solution composition, as well as to exposure time and temperature.

CHEMICALLY BONDED CONCRETE LINING IN OUTLET PLENUM AT FOUR CORNERS UNITS 4 AND 5

The Four Corners Power Plant of Arizona Public Service Company consists of five generating units fired with 0.7 to 1.0 percent sulfur coal. All five units were retrofitted with wet lime FGD systems. Units 4 and 5 were also retrofitted with baghouses for particulate control upstream of the FGD systems. The FGD systems on Units 4 and 5 consist of five spray tower absorbers, including one spare, per unit. The five absorbers discharge scrubbed flue gas into a common outlet plenum. About 18 to 20 percent of the flue gas, at a temperature of about 220°F (104°C), is bypassed through the outlet plenum to reheat the scrubbed gas from about 120°F (49°C) to about 140°F (60°C). The ductwork configuration resembles Type II (refer to Table 2).

The outlet plenum of each unit is a circular carbon steel duct with abrupt increases in diameter just upstream of the first (north) and third (center) absorber tower exits. The carbon steel is lined with a mica flake-filled polyester membrane, with a nominal thickness of 40 mils, under a potassium silicate bonded concrete with a nominal thickness of 2 in. The membrane was spray applied and the concrete was gun applied with mix water added at the nozzle.

Some problems have occurred with the gunite lining. Softening and debonding have been observed on one face of vertical turning vanes at the north and north center absorber towers; the affected area is about 1,000 ft². Some cracking of the lining has been observed at other locations. Extensive samples of the gunite lining and membrane were available from four locations in each unit. Representative samples from each location were obtained for analysis, along with duct condensate samples.

The results of the condensate analyses are shown in Figure 3 along with a calculated temperature profile for the outlet plenum. The concentrations of acidic species (Cl⁻, F⁻, and SO₄⁻²) appear to correlate with the expected condensation temperatures for these species, e.g., the drastic increase in chloride concentration beginning at the center module. The molar ratios of fluorine to aluminum are 1.3 at Module 4N and 2.6 at Module 4C, indicating that the amount of free fluoride is minimal assuming that the source of aluminum is fly ash rather than the gunite lining. The condensate samples were collected from the outlet duct damper drains and, thus, should not be contaminated with leachate from the gunite lining.

Measurements of apparent porosity and bulk density of gunite samples from selected outlet plenum locations showed that there was no significant gradient in the values of these physical properties as a function of sample depth. Therefore, there was no indication of degradation of the gunite. Samples from the same selected locations were subjected to chemical analysis for Ca, K, Cl, F, P, and S. The concentration profiles for Cl, F, and S indicated that the gunite lining was penetrated from both the exposed surface and the surface at the interface with the organic membrane. Apparently, condensate seeped through cracks and/or pores in the gunite and accumulated at the interface. The data also indicated some penetration of calcium salts into the gunite lining. The concentrations of K and P were consistent among the samples and their concentration profiles were relatively flat. These data were as expected because K and P are original constituents of the gunite. There was an apparent

buildup of P on the exposed surface of the gunite, indicating that phosphate hardener may be leaching from the binder phase.

Previous EDS analyses of organic membrane samples (6, 7) showed that Cl had penetrated to the steel substrate and that Fe from the steel was back-diffusing into the membrane. These results were confirmed by WDS analyses which also detected the presence of fluorine in the membrane. However, subsequent analysis of mica flakes from an unexposed and an exposed membrane sample demonstrated that the fluorine was originally present in the mica.

The performance analysis indicated that there was no significant deterioration of the gunite in the samples provided. The deterioration previously reported was probably due to the use of off-specification material, improper application, or improper curing in the affected areas. The gunite is being penetrated by condensate which, in turn, is penetrating the organic membrane and causing corrosion of the steel substrate. Eventually, the organic membrane will fail by adhesive debonding.

GLASS FLAKE-FILLED POLYESTER LINING IN STACK BREECHING AT PETERSBURG UNIT 3

Petersburg Unit 3 of the Indianapolis Power & Light Company is fired with 3.0 to 4.5 percent sulfur coal. This unit has a wet limestone FGD system with four absorber modules. Each absorber is designed to scrub about 25 percent of the flue gas at full load so that there is no spare module. Flue gas from the combustion air preheater flows through two symmetrical gas paths to the stack. Each path contains an electrostatic precipitator, an induced draft fan, a booster fan, two tray tower absorbers, an outlet plenum, an indirect hot air reheat system, and a stack breeching. Scrubbed gas is mixed with hot reheat air in the outlet plenums, and then further reheated by mixing with bypassed flue gas in the stack breechings. The ductwork configuration resembles Type IV (refer to Table 2).

The breechings (and the flue) are carbon steel lined with a glass flake-filled polyester. The lining failed a relatively short time after application. The normal operating temperature downstream from the bypass junctions is 160 to 180°F (71 to 85°C). However, if the FGD system is off-line, the temperature can be as high as 320°F (160°C).

An inspection of the lining was difficult to perform due to considerable deposits on the duct walls. However, close examination of several portions of the walls indicated that many sections of the lining had debonded and were missing. The exposed carbon steel substrate showed corrosion, but there was not a large amount of metal loss.

X-ray diffraction (XRD) analysis of lining samples indicated that rutile (TiO_2) was definitely present, and natrojarosite [$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$] and hematite ($\alpha\text{-Fe}_2\text{O}_3$) were most likely present. The rutile is probably a filler in the polyester resin, but the source of the hematite is uncertain. Natrojarosite is definitely a foreign compound, i.e., not originally present in the lining. In a previous failure analysis of a mica flake-filled polyester flue lining at Duck Creek, it was found that the mica had reacted with flue gas condensate to form jarosite deposits on the flakes (8). These deposits may have caused debonding between the mica flakes and the resin and, thus, the delamination that was observed within the lining.

SEM/EDS analysis of cross sections of lining samples (refer to Figure 4) from the breeching wall at Petersburg revealed high concentrations of Si, Ca, Na, and Al in the glass flakes. These elements are normal constituents of the flakes. Elements that were found at high concentrations in the resin included Cl, Si, and Ti. The Cl, presumably from condensate, had diffused completely through the lining. The Si and Ti are thought to be fillers in the resin; the presence of Ti is consistent with the identification of rutile in the XRD analysis. In one case, it appeared that deposits had formed on the glass flakes. EDS analysis of the deposits indicated the presence of Si, Cl, Ca, S, Na, Al, and Ti. The absence of Fe negates the possibility of the deposit being natrojarosite.

The performance analysis indicated that the lining failed by extensive debonding from the substrate (adhesive debonding) due to temperature excursions. However, IR spectroscopy indicated that the lining had started to deteriorate from acid hydrolysis. Also, soluble species, e.g., chlorides, had diffused into the lining and would have eventually caused deterioration of the lining-substrate interface. Although there was evidence of deposits on the glass flakes and insoluble foreign compounds in the lining, there was no sign of delamination within the lining (cohesive debonding).

FLUOROPOLYMER LINING IN FLUES AT BRUCE MANSFIELD UNITS 1 AND 2

The Bruce Mansfield Power Plant of Pennsylvania Power Company consists of three 825 MW generating units fired with 3.0 to 4.3 percent sulfur coal. The units are equipped with magnesium promoted, wet lime FGD systems. Units 1 and 2 have two-stage venturi scrubbers, six modules per unit, for removal of both fly ash and SO₂. These FGD systems have no bypass ducts and operate without reheat so that the ductwork has a Type I configuration (refer to Table 2).

Units 1 and 2 each have two flues and all four flues are in a common stack. Three of the four carbon steel flues are lined with a fluoropolymer. In flue 2B the lining was applied in stages, i.e., a center section was lined first and the remainder of the flue was lined during the next outage. At that time, the center section was washed with a solvent and spray coated with an additional 7 to 10 mils (0.18 to 0.25 mm) of fluoropolymer. About one year after application, numerous bubbles and blisters were observed in the lining especially in the center section (refer to Figure 5). The bubbles and blisters were mostly between the top coat and the lower coats of the lining.

A 2 ft by 2 ft (0.6 m by 0.6 m) piece of the flue was removed from the center section and subjected to a performance analysis. An unexposed panel of the same material and same size was also provided for comparison purposes. SEM examination of cross sections of the unexposed lining showed that the lining was in good condition, but there was some adhesive debonding from the substrate, presumably due to poor application. EDS analysis indicated a high concentration of lead due to the addition of lead oxide to scavenge the HF that is released during the curing cycle. Silicon, Al, Fe, K, Mg, and Ni were also detected in the unexposed lining. Presumably, these elements are present in compounds that were added as filler to improve the mechanical properties of the fluoroelastomer.

SEM examination of an apparently good region of the exposed lining revealed areas of cohesive debonding, especially the top 15 to 20 mils (0.38 to 0.51 mm). The elemental composition of the exposed sample was essentially the

same as the unexposed sample. Considerable deterioration of the exposed lining was observed at the top surface over a weld. Since fly ash particles were observed on the surface, the deterioration may be the result of fly ash erosion of the protuberance over the weld.

IR spectroscopy indicated that the lining is a mixture or copolymer of tetrafluoroethylene (TFE) and vinylidene fluoride (VdF). A comparison of the spectra of the unexposed and exposed samples indicated preferential attack of the TFE at the surface of the exposed sample. This was evidenced by the replacement of the C-F structure by C=O and/or C-C structures. The preferential attack of TFE is a surprising result since one would expect this structure to be far more stable than the VdF structure.

The results of the performance analysis indicated that the fluoropolymer lining is subject to bubbling and blistering near the surface, adhesive and cohesive debonding, surface deterioration, and preferential attack of the TFE component. However, adhesive debonding was observed only in the unexposed sample, and cohesive debonding may be related to the solvent washing of the lining in the flue before the top coat was applied. Surface deterioration was observed only in a protuberance over a weld, and preferential attack of the TFE is most likely only a surface phenomenon. The bubbling and blistering may be due to curing at too rapid a rate and/or incomplete curing. In both cases, excess HF that is not absorbed by the lead compounds can cause the bubbling. However, in the former case, these bubbles would have been noticeable before start-up of the unit. Finally, it should be pointed out that the lining is exposed to a relatively mild environment (scrubbed gas only).

DISCUSSION AND CONCLUSIONS

The results of the performance analyses are summarized in Table 4. The performance ranged from complete failure of the glass flake/polyester breaching lining because of temperature excursions during bypass operation (3-0-2 service environment; refer to Table 1) to relative success with the fluoropolymer flue lining exposed only to scrubbed flue gas (1-1-1 service environment). However, problems occurred even in the latter case probably because of improper application procedures. While service environment is always an important factor, the former case also points out the importance of materials specifications, while the latter case highlights the importance of application procedures.

Since polyester resin has a temperature limitation of 180°F (82°C), the polyester lining cannot be expected to withstand exposure to bypass gas at 320°F (160°C). Linings for FGD system components should be selected for the most severe possible service conditions. That is, if a bypass duct exists, at some time or other full bypass will occur.

Although the outlet plenums at Four Corners are exposed to flue gas at a temperature of at least 220°F (104°C), the polyester lining did not exhibit thermal damage. This lining is insulated by the gunite overlay. However, it is generally not a good idea to use a gunite lining in an FGD system outlet duct. The gunite can easily be penetrated by acidic condensate that can accumulate at the underside and corrode the substrate. If there is no organic membrane, corrosion of the steel substrate can occur immediately. A membrane will delay the corrosion, but eventually the membrane will also be penetrated by the condensate. Repairs will be expensive due to the need to remove the gunite lining.

It should be recognized that all organic linings will eventually be permeated by condensate. The time required for the condensate to reach the substrate depends upon the temperature, the chemical composition of the condensate, the type of lining, and the thickness of the lining. Battelle recently began a study for EPRI with the objective of determining the role of many of these variables in the performance of linings in FGD outlet ducts.

Rubber linings represent a special case with regard to their performance in FGD systems. Rubber has several advantages including resistance to chemical attack and abrasive wear. However, natural rubber linings have failed in the relatively mild environment inside FGD absorbers. It can be argued that the failures occurred because the rubber did not meet specification guidelines. However, even the rubber from an electric lineman's glove did not pass the recommended screening test for FGD rubber. More research is needed on specification guidelines for rubber linings in FGD systems.

When specifying a red shale or fireclay brick lining, one should insure that the chemical environment does not include uncomplexed fluoride. Perhaps more importantly, design engineers should recognize that allowances must be made for the moisture expansion that these types of bricks undergo. Moisture expansion of bricks is irreversible and highly dependent upon service conditions. Although some data exist (4), more research is needed on the magnitude of moisture expansion as a function of exposure conditions and exposure time. Moisture expansions greater than 0.15 percent have been measured in bricks that have been removed from power plant flues.

The astute use of nonmetallic linings in FGD systems can result in lower levelized costs. However, care must be taken to select a lining that is suitable for the most severe service conditions possible in a given system. The limitations of the various linings should be recognized and the maintenance cost over the life of the plant should be considered when comparing different materials choices. In many cases, a cost analysis will show that lined carbon steel is the best choice for a specific application.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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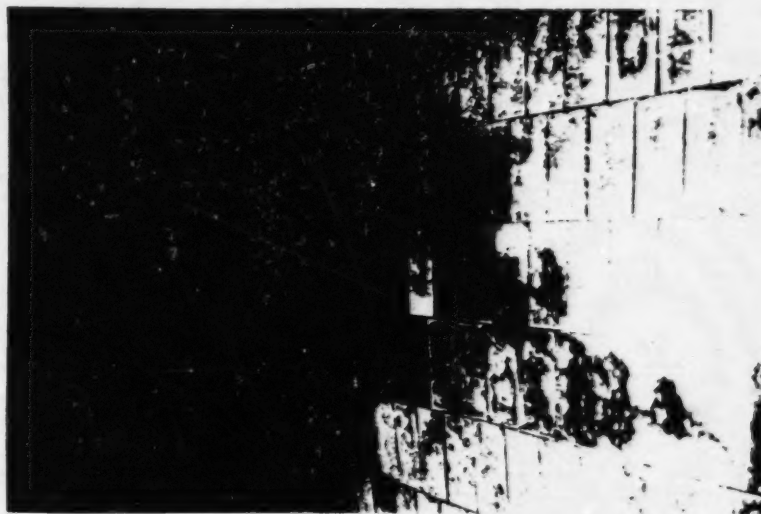


Figure 1. Major bulge in brick lining in prescrubber sump.

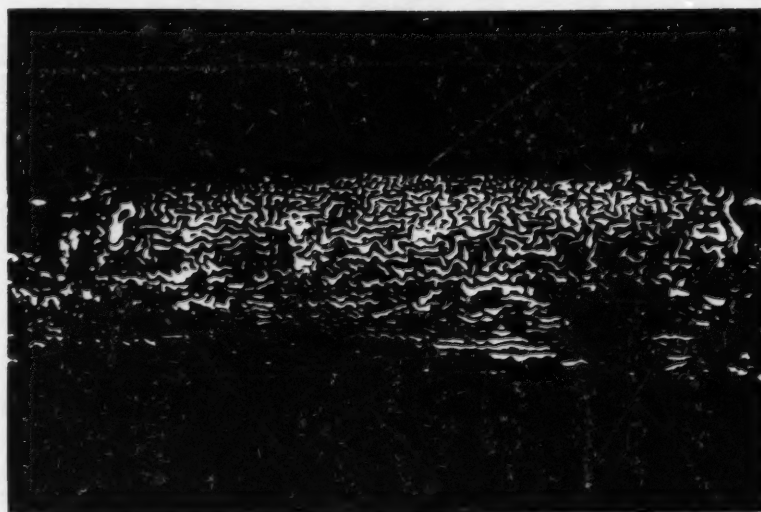
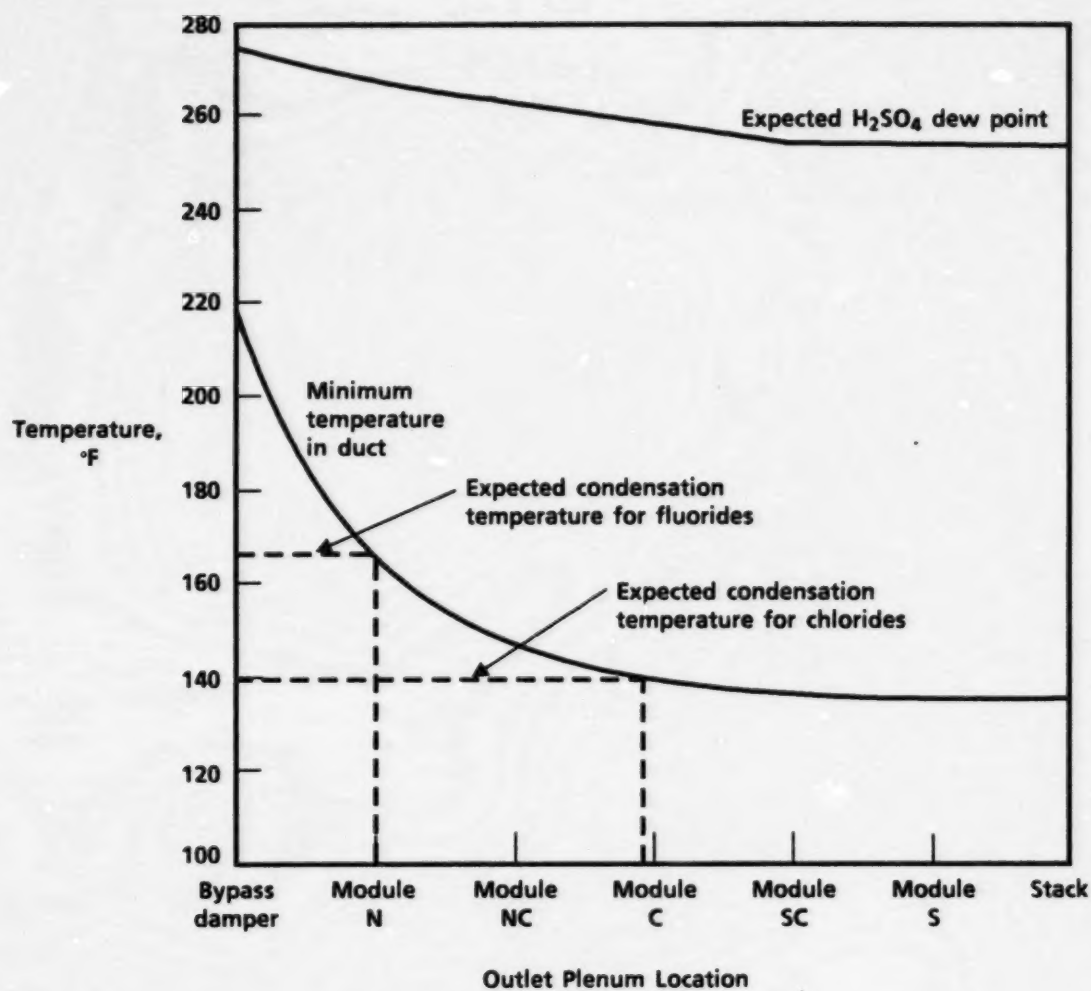


Figure 2. Rubber lining on tray support beam in absorber.



pH	4.0	~4.2	~5.4
Species	Concentration (ppm)		
Al	81	29	
Ca	220	520	--
K	2350	4925	--
Mg	400	1500	--
Na	375	850	--
Cl	220	3250	1600
F	77	52	--
SO ₄	2875	2750	2500

Figure 3. Temperature profile and condensate analyses for outlet plenum on Four Corners Unit 4.



Figure 4. SEM photomicrograph of cross-section of glass flake-filled polyester lining in breaching. (Note scale deposit on exposed surface which is at left.)



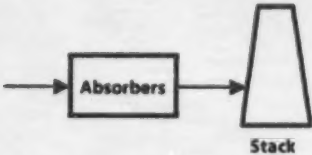
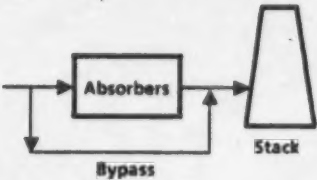
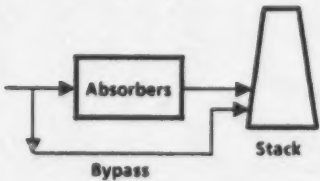
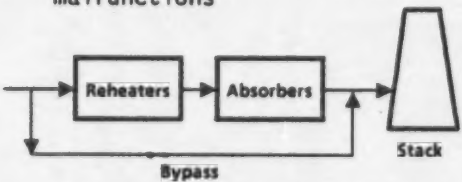
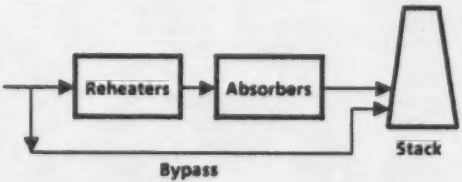
Figure 5. Typical bubbling of fluoropolymer lining in flue.

TABLE 1. CLASSIFICATION SYSTEM FOR ENVIRONMENTAL FACTORS*

Level of severity	Environmental Factor		
	Temperature	Chemistry	Abrasiveness
1	Ambient to 140°F (60°C)	pH 3 to 8 with low concentrations of fluoride and chloride	Low velocity fluid flow
2	140 to 200°F (60 to 93°C)	pH 0.1 to 3 with up to 1,000 ppm F and 10,000 ppm Cl	High velocity fluid flow, slurry sprays, or gas flow with entrained particulates
3	Above 200°F (93°C)	Greater than 15% acid with high concentrations of fluoride and chloride	High energy fluids with entrained particulates

*Adapted from Reference 3.

TABLE 2. SERVICE CONDITIONS IN OUTLET DUCTS AND FLUES

Ductwork configuration	Service Conditions*		Comments
	Outlet duct	Flue	
Type I - No reheat and no bypass 	1-1-1	1-1-1	Exposure only to scrubbed gas
Type II - Bypass to outlet duct for reheat and/or malfunctions 	1-1-1 1-1-1† and 2-2-2‡ 0-0-0† and 3-0-2‡	1-1-1 2-2-2 3-0-2	No bypass Partial bypass Full bypass
Type III - Bypass to stack for reheat and/or malfunctions 	1-1-1 1-1-1 0-0-0	1-1-1 2-2-2 3-0-2	No bypass Partial bypass Full bypass
Type IV - Operational reheaters; bypass to outlet duct for malfunctions 	2-1-1 2-1-1† and 2-2-2‡ 0-0-0† and 3-0-2‡	2-1-1 2-2-2 3-0-2	No bypass Partial bypass Full bypass
Type V - Operational reheaters; bypass to stack for malfunctions 	2-1-1 2-1-1 0-0-0	2-1-1 2-2-2 3-0-2	No bypass Partial bypass Full bypass

*Three digit codes denote severity of temperature, chemistry, and abrasiveness, respectively. Refer to Table 1 for a description of the code. A zero denotes that a condition does not exist or is not applicable.

†Upstream from bypass junction.

‡Downstream from bypass junction.

TABLE 3. IMMERSION TEST RESULTS FOR RUBBER LINING FROM SOMERSET ABSORBER

Immersion liquid	Weight Increase After 30 Days (percent)	
	125°F (52°C)	180°F (82°C)
Distilled water*	51	135
H ₂ SO ₄ , 0.015 percent		214
H ₂ SO ₄ , 5 percent		10
H ₂ SO ₄ , 5 percent/distilled water†		240
Somerset absorber liquor	15	33
NaCl, 500 ppm Na	27	
Na ₂ SO ₄ , 500 ppm Na	26	
Na ₂ B ₄ O ₇ , 200 ppm B	30	
MgCl ₂ ·6H ₂ O, 1000 ppm Mg	17	
MgSO ₄ , 1000 ppm Mg	21	
CaCl ₂ , 2500 ppm Ca	30	
CaSO ₄ , saturated	39	

*The recommended maximum weight increase after 30 days in distilled water at 180°F (82°C) is 20 percent (5). The weight increases for an electric lineman's glove after 30 days in distilled water were 6.7 percent and 22 percent at 125°F (52°C) and 180°F (82°C), respectively.

†Immersed for 30 days in 5 percent H₂SO₄, then leached to remove acid, and immersed for 30 days in distilled water.

TABLE 4. SUMMARY OF PERFORMANCE ANALYSES FOR LINING IN FGD SYSTEMS

FGD component	Lining	Service environment*	Performance features	Probable cause of problem
Prescrubber sump	Acid-resistant brick and carbon-filled furan mortar	1-2-2	Brick corrosion Bulging walls	Fluoride attack Moisture expansion of the bricks
Absorber	Natural rubber	1-1-1	Swelling	Permeation by absorber liquor
Outlet plenum	Chemically bonded concrete over mica flake/polyester	2-2-2 and 3-0-2	No deterioration of the gunite Corrosion of the carbon steel substrate	-- Penetration of the gunite and membrane by acidic condensate
Stack breeching	Glass flake/polyester	2-2-2 and 3-0-2	Adhesive debonding Deterioration	Temperature excursions Permeation by acidic condensate
Flue	Fluoropolymer	1-1-1	Bubbling and blistering	Too rapid curing and/or incomplete curing

*Three digit code denotes severity of temperature, chemistry, and abrasiveness, respectively. Refer to Table 1 for a description of the code. A zero denotes that the factor is not applicable.

THE FGD CHEMISTRY VIDEO SERIES

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ABSTRACT

For EPRI, Radian Corporation is producing a series of 15-minute videotapes on various aspects of FGD system operation, chemistry, and troubleshooting. Designed as training tools, these tapes are aimed at utility managers, FGD system operators, and technicians. The goal of the tapes is to provide operators with information they can use to optimize system performance, increase reliability, and reduce costs. Four tapes have been completed so far, with a fifth currently in production. The topics covered include basic introductions to limestone and magnesium-enhanced lime FGD systems, sampling procedures for limestone systems, performance indicators (limestone utilization and sulfur dioxide removal), and water management. The entire series eventually will include 10-15 tapes.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

I'm going to tell you about a new kind of video, produced not for MTV but for FGD. For the Electric Power Research Institute (EPRI), Radian Corporation is producing a series of 15-minute videotapes covering various aspects of FGD system operation, chemistry, and troubleshooting.

Designed as training tools, these FGD videos are aimed at utility managers, FGD system operators, and technicians. The goal of the training is to provide operators with information they can use to optimize system performance, increase reliability, and reduce costs.

The idea for the FGD training tapes began with a series of FGD chemistry and operations seminars sponsored by EPRI beginning in 1983. During these seminars, many of the results of EPRI's FGD Chemistry Program were presented. Eventually the seminars became the basis for the FGD Analytical Methods Handbook. Although they were valuable to those who attended, the seminars reached only a limited segment of the utility audience. Videotapes seemed an excellent way to convey and illustrate the seminar material and easily disseminate it to a larger audience.

We have produced four tapes so far, with a fifth now in production. Two are basic introductions to FGD systems: "Introduction to Limestone FGD" and "Introduction to Magnesium-Enhanced Lime FGD." Another is a "how-to" tape that guides the viewer through basic sampling procedures for a limestone system. The fourth is the first of several tapes on performance indicators, and covers limestone utilization and sulfur dioxide removal. The newest tape covers plant and FGD water management.

The entire video series eventually will include 10-15 tapes on topics ranging from a basic overview of existing FGD systems to FGD system troubleshooting (including some case studies), to using some of the FGD computer tools developed under EPRI sponsorship.

As you will see in the excerpts to follow, the tapes were shot on location at various coal-fired generating stations. We used video animation to complement the live action by illustrating abstract concepts. For instance, animation is especially effective at explaining chemical reactions and showing what goes on inside various process equipment.

A team of Radian engineers and chemists with considerable hands-on experience participates with EPRI in the writing of each script. These individuals also review storyboards of the animation before it is created to make sure that all the movements are technically accurate.

At each utility where we shot, we used individuals on camera to explain how they have benefitted from understanding the chemistry of their FGD system. We've gotten excellent cooperation at the plants, usually with many volunteers for starring roles.

We have already videotaped at Central and Southwest Services' Oklaunion Station, West Penn Power Company's Mitchell Station, Pennsylvania Power's Bruce Mansfield Plant, Southwestern Electric Power Company's Pirkey Power Plant, and Texas Utilities Electric Company's Martin Lake Station. We will be taping at Tampa Electric Company's Big Bend Station in November. In addition, Utah Power and Light allowed us to use still photos of one of their plants.

The response to these tapes has been very positive. EPRI has distributed over 450 tapes to utilities across the country. An EPRI survey, conducted at the time the first limestone tapes were distributed, revealed that individuals at all levels from manager to technician have found useful information in the tapes.

And even utilities without FGD systems have requested tapes, presumably to learn more about FGD before they purchase systems. Several educators also have expressed an interest in incorporating these tapes into their chemistry curricula.

The tapes have been well received by the professional video community as well. "Introduction to Magnesium-Enhanced Lime FGD" recently won a Merit Award in the Society for Technical Communication's International Audiovisual Competition.

Because it is impossible to cover a subject in-depth in 15 minutes, workbooks have been prepared to accompany and expand on the information covered in the tapes. These workbooks are designed to be studied after viewing each tape and provide additional sources of written information available from EPRI.

The following clips, pulled from three tapes, "Introduction to Limestone FGD," "Introduction to Magnesium-Enhanced Lime FGD," and "Performance Indicators," give you a flavor of the techniques used to convey information. What you will see are not scenes in sequence, but examples of how we introduce and summarize a tape, and use animation to explain phenomena such as gas/liquid mass transfer and scaling.

CHEMICAL ADDITIVES FOR DRY FGD SCRUBBERS

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ABSTRACT

The efficacy and value of chemical additives were evaluated in the Flue Gas Desulfurization (FGD) dry scrubber at a western electric power generating utility. The spray dryer scrubber incorporates both lime and fly ash as alkali reagents to meet a 0.2 lb/million BTU SO_2 state emission standard.

Data analyses have shown significant reductions in lime feed with chemical additives at equivalent MW and inlet SO_2 levels. Additive A, specifically designed to increase normally non-reactive fly ash alkali utilization, resulted in an 18% lime reduction at 15 ppm. Additive B, a formulation for enhancing general reagent utilization, produced a 15% lime reduction at 15 ppm. Concurrent reductions of fly ash slurry feed were 2% and 9% for Additives A and B, respectively.

With chemical treatment, an increase in the fraction of time within SO_2 emission compliance was obtained. NO_x emissions were also reduced by 3–5% during chemical feed. Both additives showed good performance earlier in wet scrubbers, and this evaluation demonstrates their value in dry systems.

INTRODUCTION

GENERAL SYSTEM DESCRIPTION

The plant is a three-unit, 1650-megawatt (MW) total, coal-fired electric power generating utility. This utility burns sub-bituminous coal with an average heat value of 8,300 BTU/lb and sulfur of 0.35% on a wet basis.

UNIT 3 DRY SCRUBBER

Unlike Units 1 and 2, Unit 3 employs a dry scrubber for cleaning SO_2 in the flue gas. The scrubber was designed by Babcock and Wilcox¹ and has been in service since November 1982. A scrubber system diagram is shown in Figure 1. This 550 MW Unit has four spray-dry reactors. Each reactor is equipped with 16 atomizers. Two alkali slurries, fly ash and lime, at pH 11–12 are used to remove SO_2 in the flue gas.

Flue gas enters the reactor typically at 270–310°F, contacts the lime and fly ash slurry spray droplets, and then leaves the reactor at 160–170°F. The residence time of the reactor is approximately six seconds. The lighter solid particles are collected by downstream electrostatic precipitators (ESP). The heavier solids are precipitated as the reactor ash. The precipitator ash is reused to make up ash slurry, normally 6 to 10 hours after passing the reactor. The reactor ash and excess ESP ash are disposed of after collection.

Typically all four reactors and 12 atomizers per reactor are in service at high load. Lime slurry is mixed with ash slurry just before being sprayed into the reactors. Both ash and lime slurries are made in batches by the scrubber operator, with solids targets of 30–35% and 16–18%, respectively. High density slurries tend to increase pump and tank pluggage problems. High reactor hopper ash levels will result in ash-pulling problems, and the reactor will have to be taken down for cleaning. This will leave fewer reactors available for operation.

SCRUBBER OPERATION CONTROLS

The current dry scrubber control scheme involves feeding lime slurry proportionally to the inlet SO₂ concentration, and feeding ash slurry to provide further SO₂ removal and to control reactor outlet temperatures above a minimum 160°F. Lime slurry is typically added at a mole stoichiometry greater than one relative to inlet SO₂. Minimal ash collection problems are experienced when the exit gas temperature is maintained at or greater than 160°F.

The ash slurry is prepared in a mix tank, stored in the ash slurry storage tank, and then pumped at 400–450 gpm to the reactors. The residence time of ash slurry between the ash slurry pumps and reactors is approximately 30 seconds. The flow actually entering the reactors is regulated by a back-pressure valve on the ash slurry header and individual flow control valves at each reactor mix station. A higher outlet temperature set point would reduce the ash slurry spray rate if reactor inlet temperatures stay constant. Current practice with exit temperatures equal to or greater than 160°F provides dry hopper ash.

Both ash and lime slurry densities are carefully controlled by the operator. Lime flow is regulated by the inlet SO₂ level at a given stoichiometric ratio set by the operator. The lime stoichiometry is varied according to the need to meet the 0.2 lb/million BTU SO₂ emission standard. Typically, the lime stoichiometry is set from 1.2 to 2.5, requiring a total of 60–120 gpm lime flow. A higher lime stoichiometry is usually required at low MW loads (< 300 MW). The instantaneous SO₂ removal is calculated on a six minute average basis as lb SO₂ per million BTU leaving the stack, based on the stack SO₂ and O₂ monitor values. The three-hour average of lb SO₂ values must be within the 0.2 lb compliance standard, at least 90% of the time every month to satisfy the state requirement.

SYSTEM LIMITATIONS

In the past, there were difficulties in meeting the SO₂ emission standard when burning high sulfur (>0.47%) coal. Also, SO₂ emissions tend to go out of compliance when scrubber problems and boiler low exit gas temperature problems occur. Difficulties exist when one or more of the reactors is lost due to high hopper ash levels, slurry pump failures, low reactor inlet temperatures (<270°F), or slurry tank pluggage. Frequently the SO₂ emission standard is exceeded when bringing a reactor back on-line. Low lime and ash slurry densities can also cause SO₂ emission to be out of compliance.

The state NO_x stack emission standard requires 0.7 lb/million BTU for the three-hour average values, and opacity standard is at 20%. There are generally no compliance problems with stack opacity, particulate matter or NO_x emission.

The objective of the plant is to always be within the State SO₂, opacity and NO_x emission requirements as well as to further reduce these emissions. This, and the large cost savings associated with better scrubber reliability, higher lime reagent utilization, and improved scrubber availability, brought chemical treatment into consideration.

NALCO CHEMICAL TREATMENTS

Nalco's success in using chemical additive (A) for fly ash alkali utilization improvement has been documented previously². More important is the recent finding of a formulation that enhances SO₂ removal and general reagent utilization. Unlike Additive A which is specific for certain fly ash, Additive B is effective on limestone, lime, and fly ash. Since the plant utilizes both fly ash and lime as scrubbing reagents, both chemicals had a potential to improve the performance of the Unit 3 dry scrubber.

The objective of this chemical additive evaluation was to determine the additive's performance in the Unit 3 dry scrubber at the plant. Specifically desired were:

- Improve the percentage of time that the electric power utility meets SO₂ emission compliance
- Reduce lime consumption and increase fly ash utilization
- Increase the reactor outlet temperature
- Evaluate the impact on NO_x emission
- Assess chemical impact on the electrostatic precipitator and reactor ash collection
- Reduce the maintenance costs associated with the Unit 3 dry scrubber

A more cost-efficient scrubber operation for the plant should be the result.

TEST PROCEDURE

The field evaluation was conducted from April 11 to May 16, 1988. Two chemical feed methods were available. The first was to feed to the suction side of the ash slurry pumps, and the second to the ash slurry mix tank during makeup.

FEED METHOD AND DOSAGE

Feeding by the first method gave a short 30-second reaction time before going into the atomizers. The chemical dosage, calculated based on a constant ash slurry flow, is not very accurate because of flow and recycle variances. This method, however, allowed for quick termination of chemical feed had any undesirable effect such as wet solids been observed. This feed method was thus chosen as the startup feed method.

Feeding to the mix tank provided longer chemical reaction time. Chemical dosage based on fresh ash makeup is more accurate in controlling chemical performance. Varying amounts of chemical recycle were expected from the recycled ash slurry and precipitator ash.

Additive A was fed intermittently for three days to the suction side of the ash slurry pumps at 5 to 15 ppm. The feedpoint was then changed to the mix tank at 15 ppm for five days. Additive B was fed to the suction side of the ash slurry pumps at 8-15 ppm for 7.5 days. Baseline data were collected for approximately ten days after chemical feed was stopped.

SAMPLING POINT AND ANALYSIS

Thirty-two slurry samples were gathered from three sampling points:

- Point A — discharge side of ash slurry pumps

- Point B — ash slurry off B reactor just before mixing with lime into the reactor
- Point C — ash slurry off C reactor just before mixing with lime into the reactor

On-site chemical analyses were performed. Initial slurry samples were filtered with both 1.2 and 0.45 micron Millipore® pads immediately after sample collection. Later samples were filtered with 0.45 micron pads. On-site chemical analyses included soluble calcium, total hardness, aluminum, alkalinity, pH, and density measurements. Soluble calcium, hardness, and alkalinity were determined using the conventional wet methods. Aluminum ion levels were determined on-site using atomic absorption (AA) spectroscopy. Solid samples were dried in the atmosphere before shipping with the liquid samples to Nalco's Technical Center in Naperville, Illinois, for further analyses.

Both water and solids analyses were performed on shipped samples. Water analysis was performed using inductively-coupled plasma (ICP) spectroscopy. Solids analysis was conducted using X-ray fluorescence and X-ray diffraction spectroscopies. Two sets of reactor and precipitator ash samples, one during and another after chemical treatment, were also analyzed.

SCRUBBER OPERATION DATA ACQUISITION

Scrubber performance data were collected throughout the evaluation. Six-minute average values were collected. The majority of the data analysis was performed based on the summary taken every hour from a computer display. The most relevant parameters for this evaluation include MW load, inlet SO₂ level, gas inlet temperature, gas outlet temperature, ash slurry flow, lime slurry flow, lime stoichiometry, ppm SO₂ in the stack, lb/million BTU SO₂ in the stack, ppm NO_x in the stack, stack temperature, ash density, lime slurry density, and the number of reactors in service.

BACKGROUND ANALYSIS

SCRUBBER CHEMISTRY

To ensure proper selection of additives, Unit 3 scrubber ash slurry was used in the laboratory wet mini-scrubber², located at the Nalco Technical Center, to help predict additive performance. Both additives were found to improve SO₂ scrubbing efficiency (Figure 2). A dosage higher than the field dosage is usually required in the laboratory testing.

Chemical analysis (Table 1) of the scrubber slurries showed very low soluble calcium (41 ppm as calcium) and negligible magnesium. Solids analysis supports the finding of low fly ash alkali utilization, displaying high (20% as Ca) calcium and low sulfite/sulfate (9%/15% as oxide). Aluminum content in the solids was high (9%). Among the crystals identified were hydrated lime, lime, and calcium aluminum compounds. The presence of calcium aluminum compounds in both fly ash and slurry solids correlates to the improvement in fly ash alkali utilization observed with Additive A.²

SCRUBBER OPERATION

Scrubber operator's two-hour data logs for reactor and stack monitors prior to chemical feed were analyzed. The following observations were made.

1. System Dynamics

Scrubber systems are known to be very dynamic, and the scrubber at this plant is no exception. Constantly changing load and inlet SO₂ levels force corresponding adjustments in lime and ash slurry flows and other performance parameters.

2. Inlet SO₂ Levels

The readings from the two inlet SO₂ monitors did not agree. The disagreement is probably due to inequivalent positioning of the SO₂ probes in the gas flow. Also, outlet SO₂ levels at the exit of the four reactors were different. The stack SO₂, which is used for SO₂ stack emission measurements, is the most consistent and reliable among all SO₂ monitors.

3. Lime Slurry Flow vs. Inlet SO₂ Levels

Variations in lime slurry flow paralleled those of the inlet SO₂ level, as expected from the control scheme in use (Figure 3). Therefore, percent sulfur in the coal directly affects inlet SO₂, which in turn influences lime slurry flow requirements.

4. Ash Slurry Flow vs. MW

When load and inlet SO₂ are increasing, total lime slurry flow would be increased due to a higher inlet SO₂. The additional mass of SO₂ due to higher gas flow volume is compensated for by an increase of the ash slurry flow. This explains the corresponding ash slurry flow pattern with MW, as shown in Figure 4. Increasing inlet SO₂ levels were seen with increases in load.

Ash slurry flow is controlled by the outlet gas temperature at the reactor exit. Since the outlet gas temperature is related to inlet gas temperature, inlet gas temperature and soot blowing have an indirect impact on the ash flow.

INDICATORS FOR CHEMICAL-CAUSED IMPROVEMENT

Since some scrubber control variations exist, improved scrubber performance with chemical addition could be observed individually or in any combination of the following:

- A reduction of lime slurry flow while at a constant ash slurry flow
- A reduction of ash slurry flow while at a constant lime slurry flow
- An increase in exit temperature while at a constant ash and lime slurry flow

However, a true steady state condition is unlikely in a real scrubber. Improvement with chemical feed will have to be observed as a combination of these changes.

CHEMICAL PERFORMANCE

SO₂ EMISSION COMPLIANCE

One of the biggest concerns at the plant is Unit 3's SO₂ emission compliance. Based on the ten-day baseline and 7.5 days of data with additive B treatment, there were a total of 17 hours out of compliance during baseline vs. four hours during additive B feed. The percent of time meeting compliance was:

Baseline:	93.6%
With Additive B:	98.1%

The above values show an improvement in the fraction of time within compliance using chemical feed. This improvement should be monitored over a longer term. The data with Additive A feed were not analyzed this way because of insufficient treatment time and, occasionally, uncertain chemical feed rates into the system. However, they generally indicate the same improvement. Data continues to be evaluated in this on-going program.

LIME CONSUMPTION

1. Short Term

Given the dynamics and interdependency of the scrubber performance controlling parameters, short term comparisons, before and after chemical feed, can better describe the immediate impact of chemical treatment. The ability of Additive A and Additive B to drastically reduce lime flow during the first day of feed is shown in Figures 5 and 6. Lime flow was reduced from 65–70 gpm to 45–55 gpm on the first feed day of Additive A. Similarly, Additive B reduced lime flow from 75–80 to 45–55 gpm on the first day of feed. These positive responses are attributed to chemical enhancement.

2. Long Term

A longer term comparison is more meaningful. The hourly CRT summaries were used for fast data analysis. A total of 236 sets of observations were gathered for the baseline, 216 observations for Additive B, and 101 for Additive A feed periods. For the purpose of comparison at equivalent MW and inlet SO_2 levels, these data were first sorted into six limited load ranges: 200–300, 301–400, 401–450, 451–500, 501–530, and 531–550 MW. Average values were then calculated for each segment (Tables 2 and 3).

As dictated by operating conditions, most data fall in the 500–550 MW range. For comparison of untreated vs. treated systems, a minor adjustment was made to equalize inlet SO_2 levels within each MW segment. These data are labelled as corrected values. As indicated, the results give an average of 18% reduction of lime feed with Additive A, and 15% reduction with Additive B on a statistical weight basis. Additive A gave an additional 2%, and Additive B a 9% reduction in the ash flow. Total solids production was reduced 3% and 7% for Additives A and B, respectively, minimizing ash handling.

The MW vs. inlet SO_2 relationship for the six MW load segments is depicted in Figures 7 and 8 for the two chemicals. Inlet SO_2 increased with increased MW, the same as in the background analysis. The SO_2 levels at equivalent MW load were generally higher during chemical feed. This suggests that the above chemical improvement values are on the conservative side.

Reduction of lime flow at equivalent inlet SO_2 is obvious for both chemicals, as shown in Figures 9 and 10. The lime reduction with Additive A appears to increase at higher loads. Concurrent reductions in the ash flow requirement with the two additives are shown in Figures 11 and 12. Statistical analysis supports the continued good performance of the two chemicals on a longer term basis.

3. Chemistry Change

On-site chemical analysis indicates that the scrubber's performance improved with increasing soluble calcium in the ash slurry. The increased alkalinity improves liquid phase reactions with SO_2 . The amount of soluble calcium in the slurry varied over a large range (40–510 ppm as Ca). The variation was found to be dominantly dependent upon the excess lime flow used in reactor spraying 6 to 10 hours prior to sampling. Because soluble calcium in the slurry is continually changing, it is difficult to isolate the chemical-caused improvement.

Previous laboratory studies have determined different mechanisms for the two chemicals. Additive A removes alkalinity-blocking surface alumina on the fly ash, exposing hidden alkali to water. This leads to further dissolution and alkalinity. Additive B reduces the dissolution resistance of fly ash and lime particles, increasing alkalinity.

REACTOR EXIT GAS TEMPERATURE

One of the options that a scrubber operator could choose, after reducing lime and ash requirements with chemical treatment, is to increase the exit temperature set point. A higher exit gas

temperature would lower the ash slurry requirement at constant lime feed. Lime feed will be proportionally higher relative to fly ash than it was prior to treatment, but will still remain at or below untreated levels. The benefits of a higher gas exit temperature include drier solids, easier ash collection, and reduces the reactor outages due to wetting down reactor boxes.

NO_x EMISSION

Among other factors, the stack NO_x emission is a function of nitrogen content in the coal, load, inlet gas temperature, and soot blowing pattern. Load increase caused NO_x emission to increase. Also, a higher NO_x emission is often observed during soot blowing. Lower NO_x emission is obtained after soot blowing and is associated with lower inlet gas temperatures. The cycling NO_x emission which coincides with the soot blowing pattern is shown in Figure 13. Figure 13 also shows a reduction of NO_x emission after Additive A feed and the subsequent increase after chemical feed was stopped. The overall improvement caused by the two chemicals was 3-5%.

ASH COLLECTION

One frequent cause of reactor outages is ash removal problems. The plant reduces the reactors in service only when dropping load or having problems. Since there is no reason to shut down reactors at high loads, a larger number of reactors in service indicates less frequent reactor shutdowns, thus a higher reactor availability. At lower loads (200-400 MW), the number of operating reactors is reduced to maintain proper reactor gas flow and conserve reagents. An analysis of chemical impact on ash collection was performed based on reactor availability.

The average number of reactors in service in each MW segment was calculated, baseline vs. treated (Tables 2 and 3). The data indicate that at higher loads (401-550 MW), the number of reactors in operation was on an average higher with chemical feed than without. This is especially true with Additive A. With Additive B, scrubber operators operated a minimal number of reactors at low loads (e.g. two reactors at 200-300 MW). Chemical treatment helped minimize the reactors in service at low loads and maximize reactor availability at high loads.

ECONOMICS

OPTIMUM FEEDPOINT AND DOSAGE

Chemical feed to the ash slurry mix tank has three advantages over injection to the suction side of ash slurry pumps:

- It offers an accurate measure of chemical dosage based on ash slurry makeup
- The longer residence time allows more complete chemical reaction
- Feeding chemical during each ash slurry makeup is easy for operators to control

The effective chemical dosage used in this evaluation varied between 8-15 ppm based on ash slurry flow. Taking chemical recycle and flow variations into consideration, the chemical dosage can be further optimized, and is expected to be no greater than 15 ppm.

COST SAVINGS WITH CHEMICAL ADDITIVES

The most apparent benefit for chemical treatment is lime flow reduction. The plant spends approximately \$1 million each year on lime. An 18% reduction represents \$180,000 cost savings in lime alone. The concurrent ash slurry reduction seen with chemical addition can translate into extra lime savings. One can operate at the same ash flow rates, allowing further reduction of lime flow. This would produce an overall reduction of lime feed of at least 20%.

With chemical treatment, this utility plant can expect fewer operational problems with the dry scrubber. An example is shown in the graphs for lime density excursion. One occurred during Additive B feed (Figure 14), and another without chemical feed (Figure 15). With chemical treatment, the low lime density did not cause any compliance problem. A few high stack SO_2 values were immediately compensated for by operating at a few low stack SO_2 values. With no chemical feed, the low lime density situation forced Unit 3 out of SO_2 compliance for 12 consecutive hours.

In addition to an improved fraction of time within SO_2 emission compliance and reduced lime requirements, the use of chemical also allowed for more forgiving and flexible scrubber operation. These are especially important during sulfur upsets, gas temperature excursions, low-density slurry conditions, load swings, and other irregular boiler/scrubber conditions. There are also numerous cost savings involving makeup of power generation due to improved scrubber reliability/availability. Associated maintenance costs are also enormous. Since the two additives function by two different mechanisms, further improvement is anticipated by dual feed of Additive A to the ash slurry and Additive B to lime slurry.

CONCLUSION

Both Additive A and Additive B showed excellent performance in the Unit 3 dry scrubber at this electric power utility. The improved performance with chemical was quantified in:

- Greater time in SO_2 emission compliance
- Lower lime consumption
- Higher gas exit temperatures

Also, both chemicals appear to reduce NO_x emissions. No adverse effect on ESP solids collection efficiency was noted. Better scrubber cost-performance results from the use of these chemical additives.

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2. M. L. Lin, R. J. Mouche', E. W. Ekis, Jr., and P. A. Nassos, "Improvement of Fly Ash Alkali Utilization in FGD Systems," Paper presented at American Power Conference, April 27-29, 1987.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

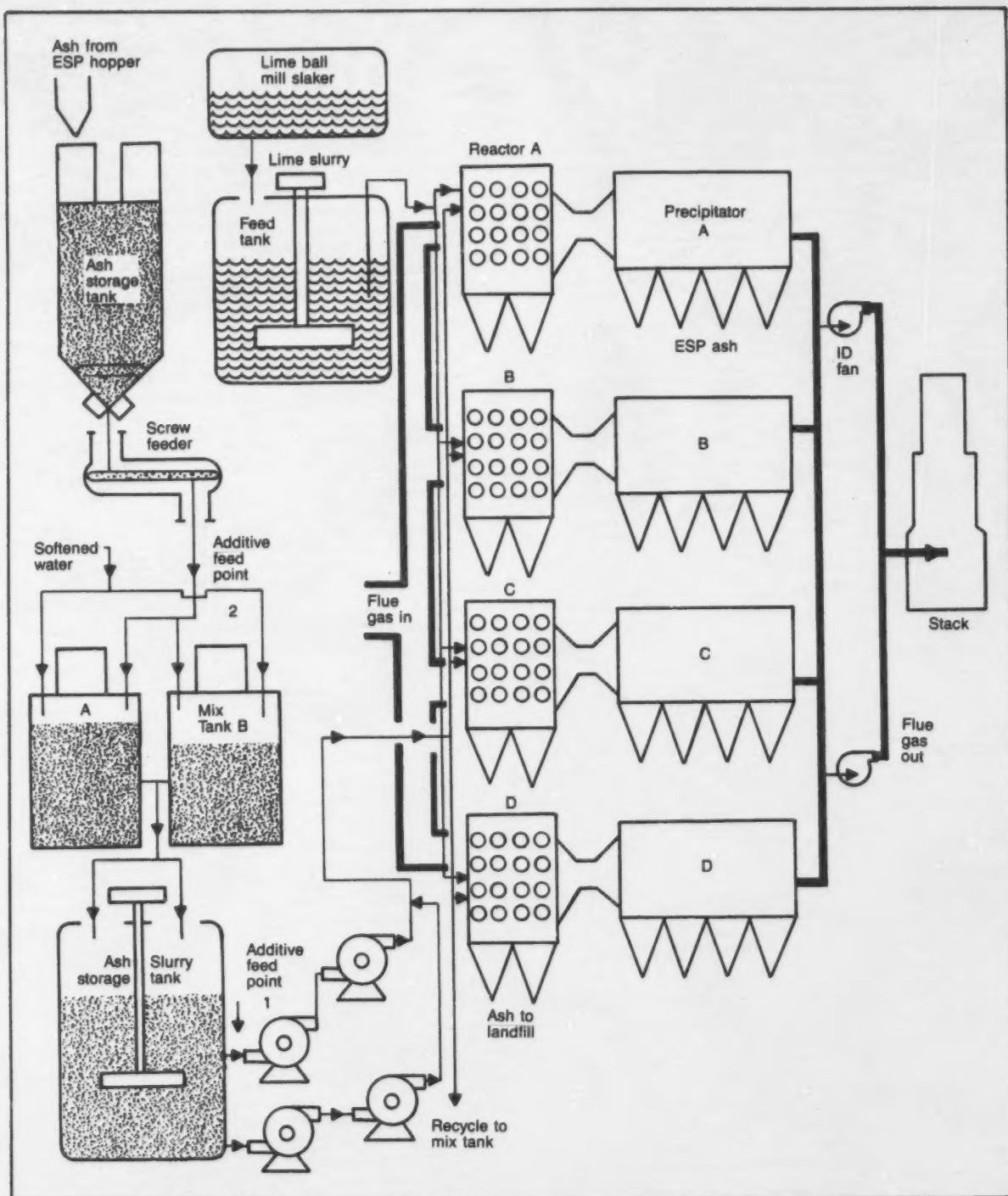


Figure 1. Unit 3 dry scrubber system

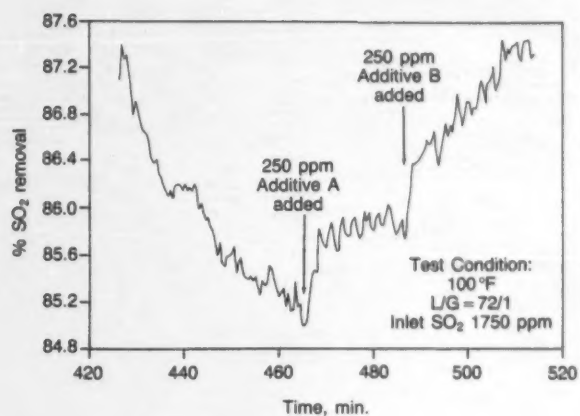


Figure 2. Laboratory scrubber simulation results

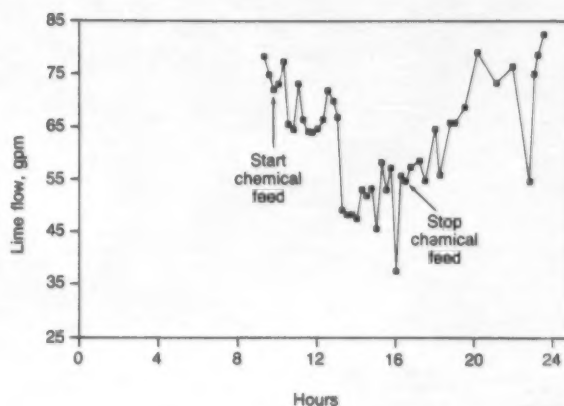


Figure 5. Short-term effect of Additive A on lime flow

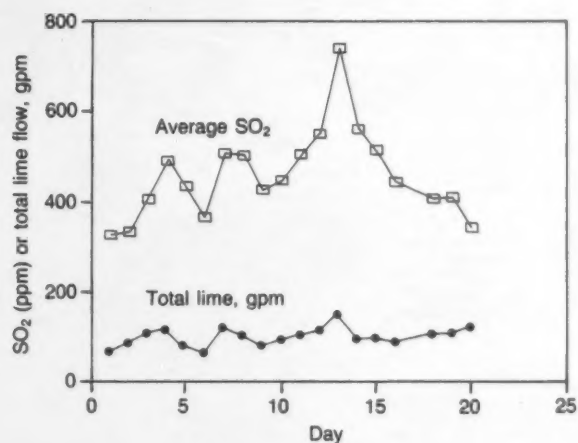


Figure 3. Baseline inlet SO_2 and total lime flow

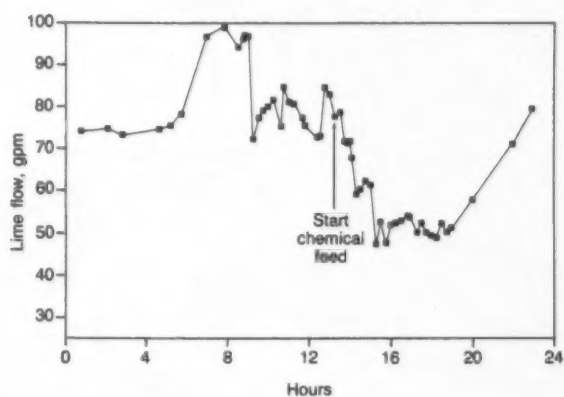


Figure 6. Short-term effect of Additive B on lime flow

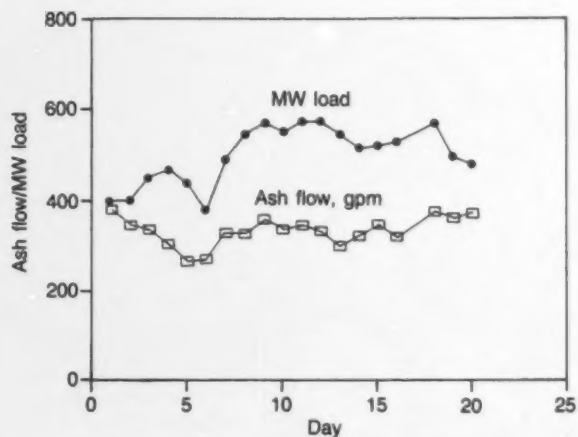


Figure 4. Baseline total ash flow and MW load

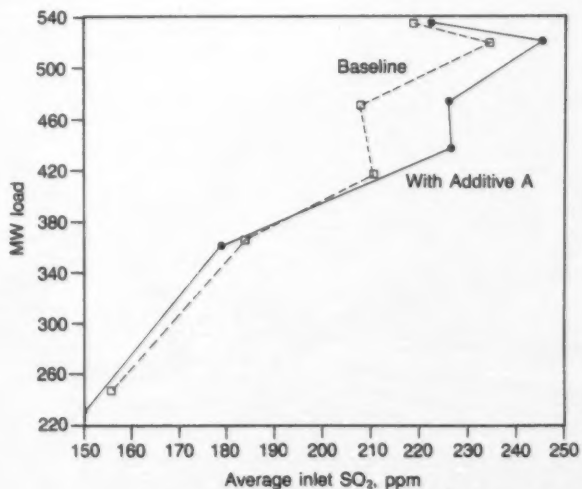


Figure 7. MW load vs. average inlet SO_2 , with and without chemical additives

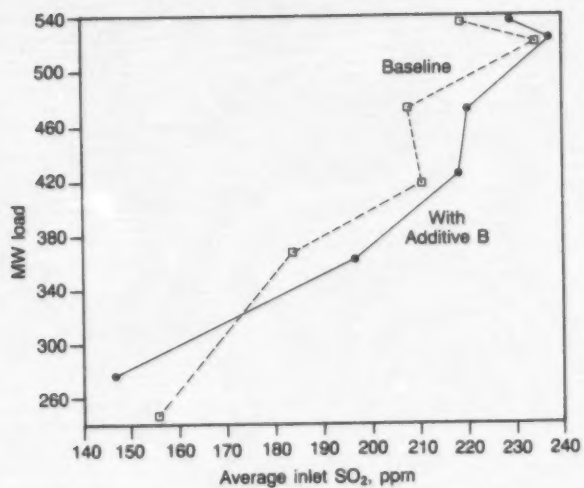


Figure 8. MW load vs. average inlet SO₂, with and without chemical additives

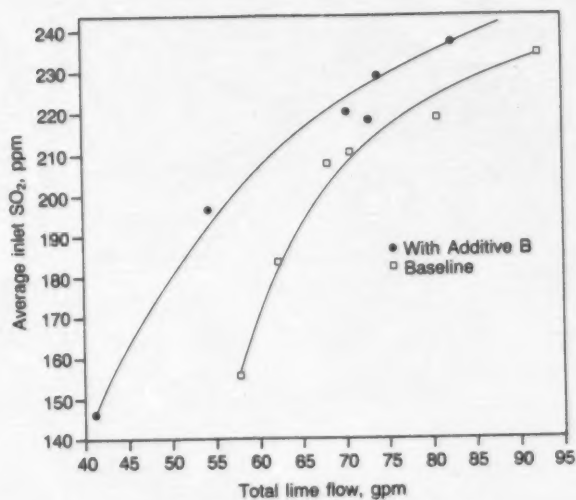


Figure 10. Inlet SO₂ vs. lime flow, with and without chemical additive

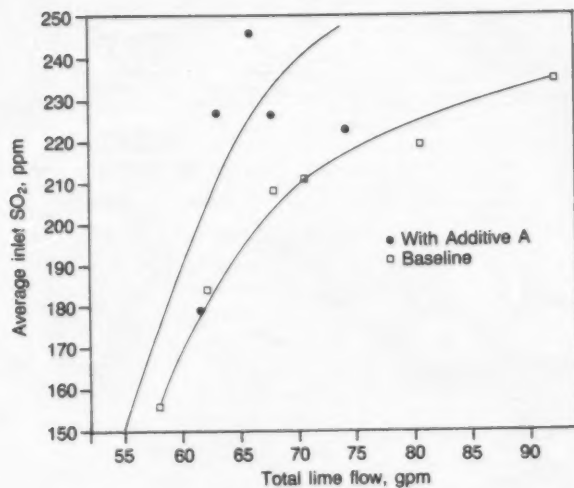


Figure 9. Inlet SO₂ vs. lime flow, with and without chemical additive

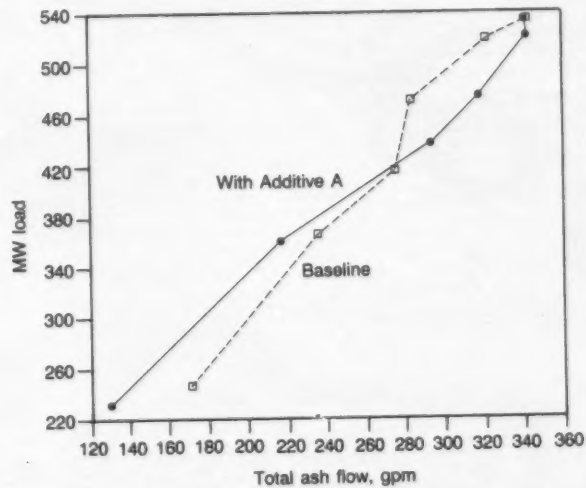


Figure 11. MW load vs. ash slurry flow, with and without chemical additive

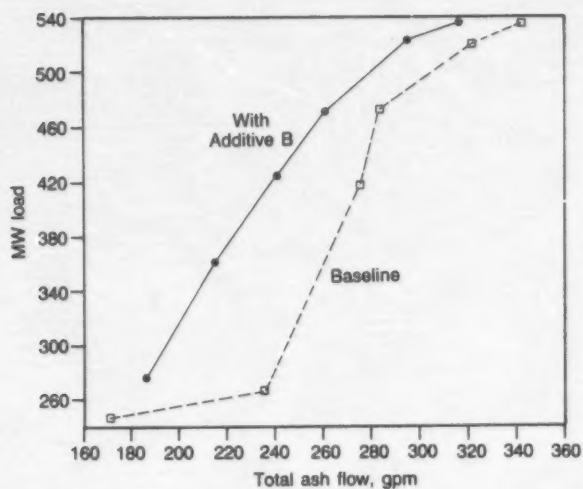


Figure 12. MW load vs. ash slurry flow, with and without chemical additive

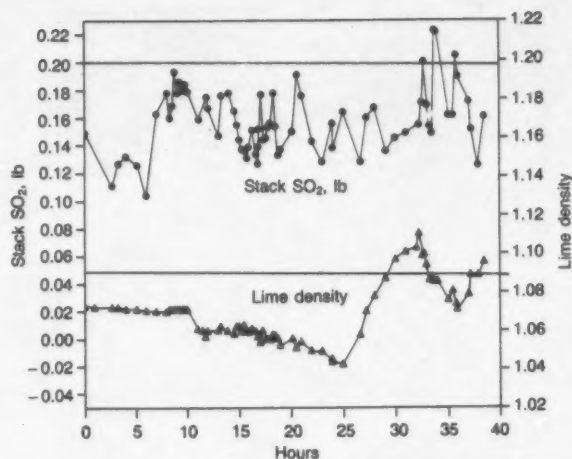


Figure 14. Low lime density with Additive B treatment

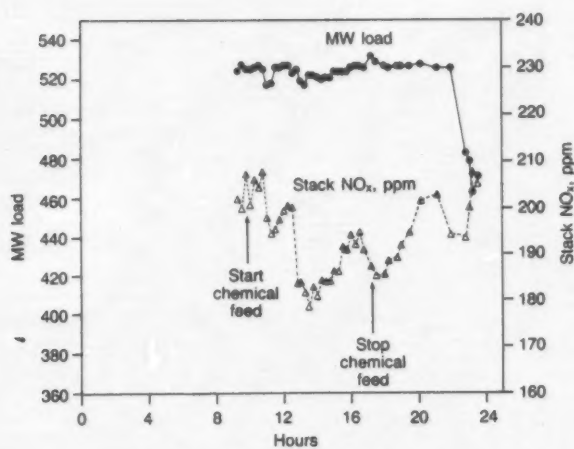


Figure 13. Stack NO_x before and after chemical feed

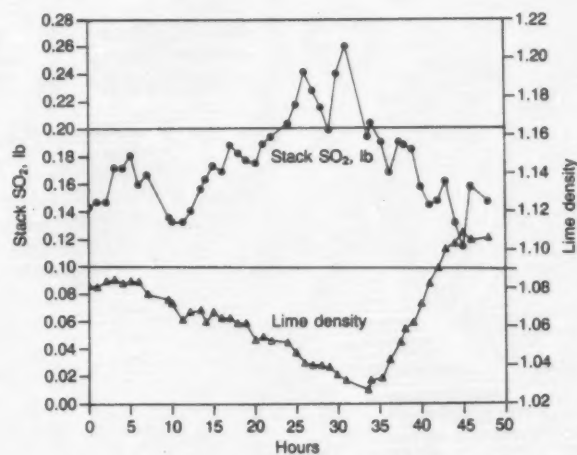


Figure 15. Low lime density without chemical treatment

TABLE 1. SCRUBBER CHEMISTRY ANALYSIS

FLY ASH ANALYSIS

	% as Oxide	Crystal Forms
Calcium	29	Silica (Alpha-quartz)
Sulfur	24	Calcium aluminum silicate
Silicon	21	Calcium hydroxide
Aluminum	9	
Iron	4	
Magnesium	4	
Sodium	2	
Titanium	1	
Phosphorous	1	

TYPICAL SLURRY WATER RESULTS

	ppm as Element		ppm as Element
Calcium	41	Sodium	1,800
Magnesium	trace	Potassium	110
Aluminum	11	Sulfur	480
Barium	3.3	Silica	61
Strontium	4.0	Phosphorous	4.5
Chromium	1.8		

TYPICAL SLURRY SOLIDS RESULTS

	% as Oxide	Crystal Forms
Calcium	30	Silica (Alpha-quartz)
Sulfur	25	Magnesium oxide
Silicon	22	Calcium aluminum sulfate
Aluminum	9	Magnesium aluminum oxide
Iron	4	Calcium silicate
Magnesium	3	
Sodium	2	
Titanium	1	
Phosphorous	1	
Barium	1	

TABLE 2. PERFORMANCE COMPARISON, BASELINE VS. TREATED WITH ADDITIVE A

MW Range	Chemical Feed	Number of Observations	Average MW	Average SO ₂ In	Average Gas Temperature In	Average Gas Temperature Out
200-300	No	15	247	155.8	262.5	162.0
200-300	Yes	6	232	150.0	256.7	161.6
301-400	No	15	367	183.8	280.6	163.0
301-400	Yes	6	362	178.8	274.3	165.5
401-450	No	7	418	210.7	284.0	163.5
401-450	Yes	6	439	226.8	285.7	165.1
451-500	No	12	473	207.9	283.0	163.3
451-500	Yes	3	476	226.3	287.1	165.4
501-530	No	54	521	234.6	290.0	162.6
501-530	Yes	45	523	245.9	289.4	162.5
531-550	No	30	536	219.0	289.4	163.4
531-550	Yes	35	537	222.8	288.6	165.0

MW Range	Average Total Ash Flow	Average Total Lime Flow	Average ppm NO _x	Corrected Ash Flow	Corrected Lime Flow	Corrected NO _x	Number of RX
200-300	171.3	57.9	135.8	160.9	57.9	127.6	2.40
200-300	130.4	53.6	133.4	130.4	53.6	133.4	2.08
301-400	236.0	62.2	174.6	232.8	62.2	172.2	3.00
301-400	217.2	61.6	156.6	217.2	61.6	156.6	2.89
401-450	275.8	70.6	189.4	275.8	70.6	189.4	3.00
401-450	293.7	63.1	174.4	279.7	58.6	166.1	3.00
451-500	283.9	68.0	184.9	282.1	68.0	183.7	3.08
451-500	318.0	67.8	181.7	318.0	62.3	181.7	3.00
501-530	321.9	92.4	186.5	321.9	92.4	185.8	3.52
501-530	342.7	66.0	186.8	341.4	63.0	186.8	3.93
531-550	342.8	80.7	192.3	342.8	80.7	191.9	3.33
531-550	341.7	74.2	179.9	340.7	72.9	179.9	3.94

TABLE 3. PERFORMANCE COMPARISON, BASELINE VS. TREATED WITH ADDITIVE B

MW Range	Chemical Feed	Number of Observations	Average MW	Average SO ₂ In	Average Gas Temperature In	Average Gas Temperature Out
200-300	No	15	247	155.8	262.5	162.0
200-300	Yes	5	277	146.8	258.9	163.1
301-400	No	15	367	183.8	280.6	163.0
301-400	Yes	14	362	196.6	273.2	162.0
401-450	No	7	418	210.7	284.0	163.5
401-450	Yes	9	425	218.5	275.1	161.6
451-500	No	12	473	207.9	283.0	163.3
451-500	Yes	16	472	220.5	286.7	162.4
501-530	No	54	521	234.6	290.0	162.6
501-530	Yes	76	524	237.5	288.3	162.8
531-550	No	30	536	219.0	289.4	163.4
531-550	Yes	96	537	229.3	290.7	163.7

MW Range	Average Total Ash Flow	Average Total Lime Flow	Average ppm NO _x	Corrected Ash Flow	Corrected Lime Flow	Corrected NO _x	Number of RX
200-300	171.3	57.9	135.8	171.3	57.9	135.8	2.40
200-300	186.2	41.2	150.5	166.0	43.7	134.2	2.00
301-400	236.0	62.2	174.6	236.0	62.2	172.2	3.00
301-400	215.1	54.3	164.2	218.1	50.8	164.2	2.86
401-450	275.8	70.6	189.4	275.8	70.6	189.4	3.00
401-450	241.1	72.8	178.0	237.1	70.2	175.1	3.11
451-500	283.9	68.0	184.9	283.3	68.0	184.5	3.08
451-500	261.3	70.2	174.1	261.3	66.2	174.1	3.35
501-530	321.9	92.4	186.5	321.9	92.4	186.5	3.52
501-530	295.3	82.4	187.6	293.6	81.4	186.5	3.51
531-550	342.8	80.7	192.3	342.8	80.7	192.3	3.33
531-550	316.8	73.8	190.0	316.2	70.5	189.6	3.44

SESSION 8: POST-COMBUSTION DRY TECHNOLOGIES

Chairman, Richard G. Rhudy, EPRI

FULL SCALE DEMONSTRATION OF ADDITIVE NO₂ REDUCTION WITH DRY SODIUM DESULFURIZATION

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ABSTRACT

Recent work in the area of dry sodium injection for flue gas desulfurization, has underscored the effectiveness of this technology for use in low-sulfur coal applications in the power industry. Dry sodium injection, however, results in increased concentrations of NO₂ in the flue gas exiting the scrubbing process. Higher NO₂ concentrations at the stack, can result in an undesirable brown plume coloration which could considerably reduce the desirability of the technology to potential users.

Several additive compounds successful in controlling NO₂ formation from sodium injection, have been identified in the laboratory and evaluated in a fabric filter pilot plant system. This paper reports results of full scale testing of three such additive compounds (urea, anhydrous ammonia, and ammonium bicarbonate) at the City of Colorado Springs R.D. Nixon Generating Station Dry Sodium Injection Demonstration Facility.

Results are presented for the performance evaluation of each additive with both sodium sesquicarbonate and sodium bicarbonate injection. Urea proved to be the most successful compound in terms of total NO₂ emissions reduction from the process. For a urea to initial NO₂ concentration mole ratio of 2, essentially 100% NO₂ reduction was observed with sodium sesquicarbonate injection and approximately 73% NO₂ reduction was possible with sodium bicarbonate injection.

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INTRODUCTION

In Phase 1 of the Dry Sodium Injection Demonstration Project at the R.D. Nixon Power Plant (completed in April 1986), injection of sodium sesquicarbonate and sodium bicarbonate in a flue gas stream prior to a fabric filter, was shown to be an effective and economical SO_2 removal technique (1). The only major problem developing from that test work was the faint reddish-brown plume that resulted at higher SO_2 removals (greater than 50%). At the time, it was theorized that the cause of the visible plume was the oxidation of NO to NO_2 .

In the last several weeks of the Phase 1 test program, injection of anhydrous ammonia in the ductwork along with the sodium sorbent was evaluated. A reduction in system outlet NO_2 concentration was detected by continuous NO_x/NO_2 analyzers, however, long term tests or trends could not be developed due to size and design limitations of the ammonia system (2).

After the Phase 1 test program was completed, Colorado Springs Department of Utilities and FMC Corporation contracted to conduct bench scale testing with various chemical compounds (3). From an earlier investigation of research in this area, it was determined that urea, ammonia, and borax were economically feasible potential additives. The tests revealed that urea and anhydrous ammonia had significant potential for reducing NO_2 , however, due to the limited test data obtained, exact stoichiometric relationships were not developed.

Additional study on the use of NO_2 reducing additives was conducted by KVB under an EPRI contract at the Arapahoe pilot facility (4). KVB conducted research with a variety of additive compounds to determine their effectiveness in mitigating the NO_2 problem. The two most successful, extensively evaluated compounds, were urea and ammonia. It was also observed that ammonium bicarbonate (ABC) exhibited high potential as a NO_2 reducing additive, but the work at Arapahoe only demonstrated its use as a SO_2 removal sorbent. Other compounds were found to be effective NO_2 reducing additives, but were rejected due to higher cost.

The preceding work led to the objective of this test program. The purpose of Phase 2 of the R.D. Nixon Dry Sodium Injection Demonstration Project was to demonstrate the use of NO_2 reducing additives on a full scale installation and compare the results with the pilot scale Arapahoe tests. The sponsors on Phase 2 of the project were Colorado Springs Department of Utilities, Electric Power Research Institute, Public Service of Colorado, and Adolph Coors Company. KVB was contracted to perform the testing and consulting services. FMC Corporation and Church & Dwight, Inc. supplied the sodium sorbents.

PROCESS DESCRIPTION

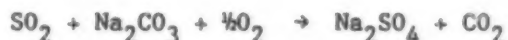
In the dry sodium desulfurization process, any number of sodium bearing crystalline compounds may be pulverized and injected directly into the coal combustion flue gas. These compounds may be sodium bicarbonate or carbonate or a combination thereof (i.e. sodium sesquicarbonate or sodium tribicarbonate). Because of proven success and commercial availability, sodium bicarbonate and sodium sesquicarbonate have been the most extensively evaluated and were the sorbents used in these tests.

Once the sorbent enters the gas stream, SO_2 and NO diffuse to the particle surface. If the gas stream temperature is below that which is required for rapid decomposition of the bicarbonate component of each material (approximately 240°F), very little SO_2 capture occurs. While SO_2 will react directly with sodium bicarbonate, in the presence of nitric oxide this reaction is inhibited and does not present an avenue for significant sulfur capture. Also, while some additional reaction with sodium carbonate in the sesquicarbonate matrix is possible, pore pluggage and product layer

buildup quickly limit the availability of fresh reactive sorbent surface.

In order that SO₂ capture (with either sorbent) may progress rapidly and attain acceptable levels of utilization, the bicarbonate component must begin to decompose. As flue gas temperature increases into the optimum range of 240 to 320°F (4), this decomposition and subsequent reaction process accelerates. When the bicarbonate component decomposes, CO₂ and H₂O are evolved from the particle interior. This off gas evolution process creates a network of void spaces throughout the particle allowing the counter diffusion of SO₂ and NO to fresh sorbent surfaces where the heterogeneous reactions take place.

It has been shown (5) that in absence of nitric oxide, the sodium desulfurization reaction product is a combination of sodium sulfite and sodium sulfate, and that the proportion of each waste material is a function of reaction temperature. However, if nitric oxide is present (as it always is in coal combustion flue gas), the reaction product is sodium sulfate alone, and SO₂ removal can be represented by the following reaction:



Lower NOx emissions also result from injection of dry sodium compounds. The mechanism by which this occurs is not well understood, but the demonstrated capability of this process to reduce NOx levels could be significant. Tests were conducted at EPRI's Arapahoe research facility to assess this NOx control potential of the process. Sodium bicarbonate was injected upstream of a pilot scale baghouse operated at 300°F. The normal subbituminous coal combustion flue gas was doped with SO₂ to vary the system inlet SO₂/NO ratio from 0.4 to 2.3 (inlet NO constant at approximately 750 ppm). As inlet sulfur dioxide concentration was increased, sodium injection was proportionally increased to maintain a nominal 70% SO₂ removal across the system. Figure 1 shows NOx removal data from this study. Clearly, as more SO₂ is reacted with the sodium compound, NOx removal steadily improves.

Since, in the absence of SO₂, nitric oxide does not react well with sodium bicarbonate or carbonate (4), it must be assumed that the reactions that produce NOx removal must depend intimately on the sodium desulfurization process. And, in fact, the pilot plant tests discussed above have shown that increasing inlet SO₂ concentration from that typical of a low-sulfur coal (300 ppm) to that typical of a 2% sulfur coal (1650 ppm) will increase NOx removal from 10% to over 30% at 70% SO₂ removal.

One serious side effect of this NOx reduction does occur, and it's solution was the primary focus of this project. In the dry sodium desulfurization process, NO is apparently oxidized to NO₂. Some, but not all of the NO₂ formed is reacted with the sorbent. Any nitrogen dioxide formed but further unreacted adds to the stack concentration of NO₂. Since NO₂ is a reddish-brown gas, it's presence can create an undesirable coloration to the stack plume. A number of additives were identified at the EPRI Arapahoe facility (4) as possessing potential in mitigating this problem. These additives were:

- anhydrous ammonia (NH₃)
- ammonium bicarbonate (NH₄HCO₃)
- urea (NH₂CONH₂)

Anhydrous ammonia appeared to aid in solution of the problem by reacting directly with NO₂ in the gas stream, and, although not previously evaluated for this purpose, it was assumed that ammonium bicarbonate would act in somewhat the same manner. Urea, however, appeared to work not only by releasing ammonia to react directly with

NO₂, but by inhibiting the actual process that produced NO₂ in the first place. While the mechanisms are still not well understood, and further evaluation would be desirable, the Arapahoe results provided the incentive to evaluate these compounds at full scale.

SYSTEM DESCRIPTION

POWER PLANT DESCRIPTION

The City of Colorado Springs Department of Utilities placed Unit No. 1 of the Ray D. Nixon power plant into commercial service on April 4, 1980. The plant is a 222-MW pulverized coal unit, and is located 17 miles south of Colorado Springs, Colorado near the city of Fountain.

The steam generator was manufactured by Babcock & Wilcox and produces a steam flow of 1,450,000 pounds per hour. The boiler is a radiant pulverized coal design with opposed-wall firing employing 21 dual-register, low-NO_x burners. The boiler utilizes subbituminous, low-sulfur coal from northwestern Colorado, but was designed for future conversion to coal supplied from Wyoming's Powder River Basin. The analyses of the coals used on Phase 2 of this project are shown in Table 1.

The particulate control equipment installed at the plant consists of two parallel fabric filter baghouses (A & B), supplied by Joy Manufacturing. Each reverse-gas cleaned baghouse has 18 compartments with 156 bags per compartment and is designed to filter one-half of the 1,071,600 acfm of flue gas at an air-to-cloth ratio of approximately 2.0 acfm/ft². The 12-inch diameter by 31'9" long filter bags are fiberglass with 10% Teflon B coating.

The plant was constructed under Subpart D of the New Source Performance Standards regulations, however, no flue gas desulfurization equipment was required, as the emission limitation of 1.2 lbs SO₂/mmBtu is easily met using low-sulfur coal.

The fly ash handling system is a pneumatic vacuum system and was also designed for the additional capacities required for Wyoming coal, and has additional storage capacity for a dry-type FGd system should it be installed at a later date. Once the ash is collected in the hoppers, it is conveyed to a 48,000 cubic feet storage silo where it is temporarily stored prior to loading into trucks for use as a concrete additive or disposal in an on-site landfill.

SODIUM INJECTION SYSTEM DESCRIPTION

The 100+ MW dry sodium injection demonstration system was designed, procured, fabricated, and erected by FMC Corporation in October 1985. The Colorado Springs Department of Utilities provided the motor controls, electrical wiring, signal wiring, and all utilities. The sodium sorbents were injected in the duct upstream of the "B" baghouse, side-by-side with the identical "A" baghouse operating without sorbent injection. For the current phase of the project, FMC Corporation provided the sodium sesquicarbonate and Church & Dwight, Inc. supplied the sodium bicarbonate.

A schematic of the dry sodium injection system is shown in Figure 2. The sodium sorbent was shipped in 25-ton bulk pneumatic self-unloading trucks. The trucks unloaded into a 100-ton storage silo located adjacent to the "B" baghouse. From the storage silo, the sorbent flowed through a bin activator and pant-leg diverter chute into two volumetric screw feeders, from which it was fed through rotary airlock valves into two separate pneumatic conveying lines. Pressure blowers supplied conveying air which carried the sorbent into two Mikropul 60 ACM pulverizers. With the discharge dampers open 100%, each blower could provide 4500 acfm at 30 in. WG of conveying air. Each pulverizer could grind an operating maximum of approximately

2500 lb/hr of either sesquicarbonate or bicarbonate. The pulverizers were equipped with variable speed separators (classifiers) to provide control of particle size. The speed range was from 600 to 1800 rpm. The sorbent particle size range possible was between 7 and 25 microns, depending on sorbent feedrate, air flowrate, and separator speed. The normal grind was between 10 and 15 microns. From the pulverizers, the sorbent was conveyed by pressure through two 12-inch carbon steel pipes to distribution headers located above the ductwork, approximately 50-feet upstream of the "B" baghouse. Vertical injection pipes came off these headers and penetrated the duct from above. The sorbent was injected into the gas stream cocurrently from injection points evenly distributed across the ductwork.

The injection system was designed to provide flexibility with respect to sorbent feed rate and distribution. The redundant feeder, pulverizer, and injection systems also allowed operation to continue while performing maintenance on equipment in one of the systems. Instrumentation included dc variable speed controllers for operating the screw feeders; a Moore process controller for automatic sodium feed control based on SO₂ mass signal; a L&N chart recorder for plant load, coal flow, flue gas temperatures, and baghouse ΔP ; a silo weight measurement system; and an alarm panel including pulverizer/separator ammeters (indicating sodium sorbent loading).

NO₂ REDUCTION ADDITIVE INJECTION SYSTEM DESCRIPTION

The NO₂ reduction additive injection systems were designed and installed by KVB and Colorado Springs Department of Utilities in April 1988. Schematics of the anhydrous ammonia additive system and the urea/ammonium bicarbonate dry additive system are shown in Figures 3 and 4.

The dry additive feed system was designed for only a two month duration and thus does not represent a truly commercial design. A K-Tron dry feed system was used that consisted of a 250-lb capacity hopper and a variable speed screw feeder mounted on a weight scale. The scale weight signal indicated on a chart recorder resulting in loss of weight versus time, thus a feedrate in lb/hr was known. The screw feeder discharged the raw urea or ammonium bicarbonate product into two compressed air venturi eductors that conveyed the additive through 2-inch flexible hoses into the sodium sorbent feed pipes upstream of each pulverizer. Thus, the raw additive was simultaneously ground and conveyed into the flue gas duct with the sodium sorbent. The additive system was capable of feed rates up to approximately 450 lb/hr. The ammonium bicarbonate was supplied by Church & Dwight, Inc. and the urea was purchased from a local fertilizer distributor. Both were supplied in 50-lb bags.

The anhydrous ammonia system consisted of a 2.2 ton liquid ammonia tank that was piped to a 150 lb/hr ammonia vaporizer unit. The gaseous ammonia from the unit then went through a control valve followed by a metering orifice and then into the 12-inch sodium conveying pipes downstream of the pulverizers. A ΔP transducer was connected to the metering orifice to determine the ammonia flowrate in lb/hr. A safety control valve was installed on the ammonia line and was designed to shut off the ammonia flow should either of the dry sodium injection blowers cut off. The liquid ammonia was purchased from a local fertilizer distributor.

CONTINUOUS GAS MONITORING SYSTEM DESCRIPTION

KVB provided a mobile laboratory test van that contained all of the gas monitoring equipment. A schematic of the equipment used on this test program is shown in Figure 5. All data from the monitors was recorded on chart recorders. NO₂ was measured from a multi-point sampling grid on the inlet and outlet of the fabric filter. Two methods were used for monitoring the NO₂ concentration. Two Thermo Electron chemiluminescent analyzers measured NO_x and NO (and thus NO₂ by difference), and a modified Dupont Model 400 photometric absorbance analyzer was used to monitor NO₂ directly. An ammonia monitoring system developed by KVB was also installed on

the baghouse outlet duct so ammonia slip could be determined during the additive injection tests. A schematic of this system is shown in Figure 6.

DESCRIPTION OF NO_x REDUCTION ADDITIVE TEST PROGRAM

Phase 2 of the Dry Sodium Demonstration Project at the R.D. Nixon power plant was organized as follows:

- 1) Boiler Baseline Testing: The initial set of tests evaluated the NO and NO_x concentrations entering the baghouse from the boiler. The effect of boiler load, excess air, and fabric filter inlet temperature were assessed.
- 2) Benchmark System with Past: Both sodium sesquicarbonate and sodium bicarbonate sorbents were tested and compared with the Phase 1 data. The sorbents were tested at various boiler loads, fabric filter inlet temperatures, and NSR's. NO_x production levels were evaluated at each of the operating conditions.
- 3) Additive Evaluation: The urea, ammonia, and ammonium bicarbonate NO_x reducing additives were evaluated with both sodium sesquicarbonate and sodium bicarbonate dry injection sorbents. The additives were tested at various boiler loads, fabric filter inlet temperatures, SO₂ removal levels, and additive to sorbent injection ratios.
- 4) Long-Term Additive Evaluation: After the parametric tests with the additives were completed, the two most effective additives (urea and ammonia) were each evaluated for week long tests with both sorbents. The tests were to confirm the additive to inlet NO_x ratios required to maintain the NO_x level under the stack visual threshold. In addition, the long-term tests made it possible to determine the economic impact of the use of additives on sorbent costs.

SO₂/NO_x REMOVAL AND NO_x FORMATION BENCHMARK TESTING

Prior to commencement of the NO_x reduction additive evaluation phase of this project, a brief benchmark test period was conducted with each sodium sorbent to compare current performance to initial sodium injection testing conducted at Nixon in 1985 and 1986 (1,2). Benchmark tests were also necessary to assess whether critical data (e.g. NO/NO_x removals and NO_x emissions) were representative of this past effort. Data obtained indicates excellent repeatability and consistency of past and current results.

Figure 7 shows SO₂ removal as a function of NSR (normalized stoichiometric ratio between the sorbent and the system inlet SO₂ concentration) for sodium sesquicarbonate injection. The figure clearly shows the consistency between past and present data. Similar data for sodium bicarbonate injection also display this level of agreement (Figure 8).

Since, for this project, NO_x emissions were the primary issue, the various relationships between NO_x compounds and other important parameters were evaluated in detail. In general, excellent agreement was observed between current and past data. Figure 9 shows NO_x and NO removals as a function of SO₂ removal for both previous and current sesquicarbonate injection test results, and although data scatter is present, satisfactory similarity in trends and absolute values are observed. There are clearly increases in NO and NO_x removals as SO₂ removal increases. Also, as SO₂ removal increases, the expanding difference between NO removal and NO_x removal may be observed from this data. This expanding difference accounts for increased NO_x emissions from the process as sulfur capture increases. Figure 10 shows NO_x

emissions as a function of SO_2 removal percent. Although data from the current project appears to be slightly lower than the past data, the NO_x emissions indicate a similar trend.

NO_x REDUCTION ADDITIVE EVALUATION

ADDITIVE INJECTION

Three compounds, urea (NH_2CONH_2), ammonia (NH_3), and ammonium bicarbonate (NH_4HCO_3) were selected for full scale evaluation to minimize the potential for a sodium desulfurization "brown plume". Two of these compounds (urea and ammonia) had met with significant success in reducing NO_x emissions from dry sodium injection pilot plant experiments (4). The third material, ammonium bicarbonate (ABC), had not been previously evaluated as an NO_x reduction additive, but was of interest because it was another source of ammonia. Also, it could easily be included in the sodium bicarbonate manufacturing process, resulting in production of a combination sorbent/additive material.

Tests were conducted over a range of additive feed rates, sorbent feed rates, and flue gas temperatures for both sesquicarbonate and bicarbonate injection. Although variable, nominal conditions for the majority of these tests were:

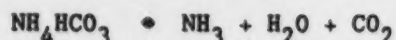
flue gas temperature = 280°F
inlet SO_2 @ 3% O_2 = 400 ppm
inlet NO @ 3% O_2 = 350 ppm
sodium sesquicarbonate NSR = 1.5
sodium bicarbonate NSR = 0.9

To establish performance curves, additive feed rates ranging from 1 to 20 percent by weight of the injected sodium sorbent were evaluated. Figures 11 and 12 show these results. The maximum feed rate tested was different for each additive. For urea, 100% NO_x removal was attained at feed rates from 11 to 12 percent. This made additional injection unnecessary. For NH_3 , the maximum addition rate was 10% (75% NO_x removal) due to a vaporizer system limitation. However, only marginal increase in NO_x removal was experienced by increasing the ammonia addition rate from 7 to 10 percent, indicating higher rates may not have resulted in additional NO_x reduction. Finally, the maximum ammonium bicarbonate (ABC) rate of 20% was dictated by mechanical throughput limitations of the dry additive feed system. NO_x removal of only 41% was observed for ABC at this maximum feed rate.

Since an NO_x concentration of approximately 30 ppm was identified as the visual threshold from the R.D. Nixon stack, reducing emissions below this level was desirable. The visual threshold for NO_x , at other locations, would depend on a number of factors and thus is site specific. For SO_2 removals ranging from 70 to 90 percent, the dry sodium scrubbing process resulted in an outlet NO_x concentration averaging 50 ppm. To be safely below the visual threshold, a reduction in NO_x of approximately 50% was required. The data in Figures 11 and 12 show that urea and ammonia were about equally effective in attaining this goal. An addition rate of approximately 3.5% of either compound resulted in 50% NO_x removal. ABC, however, was not as effective. An ABC addition rate of 3.5% only resulted in a 10% reduction of the NO_x emissions.

If NO_x removal efficiency is plotted versus additive to initial NO_x concentration molar ratio, additional information regarding each additive is revealed. This is shown in Figures 13 and 14. The data indicate that on a molar basis, ammonium bicarbonate and anhydrous ammonia are about equally effective in reducing NO_x concentrations even though one compound was injected as a pulverized solid and the other as a superheated vapor. This observation seems consistent with the fact that

ammonium bicarbonate should decompose in the gas stream (at temperatures above 120°F) to ammonia, water, and carbon dioxide by the equilibrium:



Then, since each mole of decomposing ammonium bicarbonate provides one mole of ammonia, the two additives would appear to be very similar in NO₂ removal capability. Any small differences in performance (on a molar basis) between these two compounds may be the result of physical mixing limitations in the injection system and in the flue gas ducting.

The mechanism by which urea worked appears to be different than that of ammonia and ABC. If it is assumed that heating urea at 280°F, results in the following decomposition (6):



then, one mole of ammonia results from the decomposition of each mole of urea. Direct reaction of this amount of ammonia cannot sufficiently explain the higher NO₂ removals possible (on a molar basis) with urea compared to anhydrous ammonia or ammonium bicarbonate. Other reaction mechanisms must be involved.

Overall system NO_x and SO₂ emissions were effected by additive injection. NO_x removal typically, but not always, increased with the use of each additive. Figure 15 shows comparable data for urea, ammonia, and ABC injection. For these tests, an increase in NO_x removal from 3 to 30% was observed.

SO₂ removal consistently increased for ABC and ammonia addition and consistently decreased for urea injection (Figures 16,17,18). This increase in SO₂ removal when using ammonia or ABC could explain the poorer performance of these compounds for NO₂ reduction at higher molar injection ratios. Since NH₃ has been shown to react with SO₂ in a gas phase reaction process (7), any ammonia captured by SO₂ would not then be available to react with NO₂. Increasing the injection rate of ammonia may increase SO₂ removal but not necessarily NO₂ removal.

AMMONIA SLIP

For this process, a very important consideration in the use of any additive material is how efficiently the compound is utilized, and what amount, if any, of the compound exits the system via the exhaust gas stream. To be able to determine ammonia slip rates during the injection of any of the additive compounds, a special ammonia monitor, designed and constructed by KVB (Figure 6), was included in the continuous monitoring instrumentation for this project. Figures 19 and 20 show data from this monitor during sodium bicarbonate injection. For each test, during which ammonia slip measurements were made, four data items are shown. The amount of NO₂ (ppm) actually removed during the test is represented by the first bar in each group. The second bar indicates ammonia slip actually measured by the instrument. The third bar is the sum of bars one and two, and would represent the total ammonia expected in the gas stream if only NO₂ was allowed to react with ammonia. Bar four is the calculated maximum concentration of ammonia in the gas based on the additive injection rate.

Inspection of Figure 19 (ammonia injection tests) reveals more ammonia was available in the gas stream than accounted for in NO₂ removal and slip measurements. It can be shown by calculation, that the quantity of ammonia that resulted in increased SO₂ capture, can account for the majority of this excess. Figure 20 shows a different trend for urea injection. In each test, the theoretical maximum available ammonia concentration is slightly less than the sum of the measured ammonia slip and the amount of NO₂ reduction. Considering the margin of error in these measurements and calculations, both sets of data appear to be consistent, and, at least in terms of

ammonia utilization, indicate a more efficient use of urea compared to anhydrous ammonia. Both sets of data, however, also emphasize the inefficiency of the additive injection process in terms of ppm of NH_3 emitted to the atmosphere per ppm of NO_x reduced. In an actual, continuous process application, it will be essential to optimize additive injection to reduce ammonia slip both because of the potential undesirability of ammonia emissions, and because of the increased additive cost.

FABRIC FILTER IMPACT AND EQUIPMENT PERFORMANCE

DRY INJECTION IMPACT ON FABRIC FILTER

In addition to the NO_x additive investigation, a second objective of the test program was to conduct various tests to monitor the impact of sodium and additive injection on the fabric filter. In the previous dry injection testing at Nixon (1,2), there was no significant impact on the fabric filter observed at that time. However, the Nixon plant personnel replaced considerably more bags in the "B" baghouse (the side with dry injection) than the "A" baghouse (without dry injection) during the period of time after the first project (April 1986) and the start of this project (May 1988). It is important to note, however, that the Nixon bags have been in service since the unit went into operation in April 1980. Thus, knowing that dry sodium injection increases the baghouse inlet mass loading by more than 50%, it is possible that this additional bag loading shortened the already excellent bag life when compared to the bags in the "A" baghouse. In addition, earlier lab analyses had showed no form of chemical deterioration of the bag fabric (fiberglass w/10% Teflon B coating) as a result of sodium injection.

During this test program Southern Research Institute conducted fabric filter inlet and outlet particulate mass loading tests, bag weight tests, and compartment inspections. The results showed that sodium and sodium/additive injection did not increase the fabric filter outlet particulate emissions and that no significant increase in bag weights were found due to sorbent or additive injection.

SODIUM AND ADDITIVE INJECTION EQUIPMENT PERFORMANCE

The dry sodium injection system performed very well. The primary problem with the equipment during Phase 1 of the project (completed April 1986), was buildup of the sodium compounds in the pulverizers. This phenomena occurred with both sodium sesquicarbonate and sodium bicarbonate. The buildup was in the form of a hard scale that over a period of two to three weeks of operation would begin to impact the performance of the mills. Typically, the buildup would cause a deterioration in discharge particle size by interfering with the separator, but at times it also caused the mills to reach an electrical overload condition. When the mills reached this point, maintenance personnel had to remove the top of the pulverizer and clean out the internals. The sodium scale is water soluble, but since the particular mill design has a mechanical seal under the hammer assembly, the unit would have to be disassembled to clean with a wet technique.

Based on a technique developed by Public Service of Colorado, the problem with mill buildup causing downtime was eliminated on Phase 2 of the project. The procedure involved the use of silica sand to clean the mill internals. Approximately every two to three weeks, without effecting operation, 200 to 300 pounds of sand was run with the sodium product through the mills. This procedure eliminated any large buildup that could effect mill performance.

Another important operational characteristic that must be considered when designing a dry injection system, is the flow properties of the sorbents used. During the Nixon tests, sodium sesquicarbonate demonstrated superior handling characteristics compared to sodium bicarbonate. Using the same type of bulk self-unloading trucks, 25-tons of

sodium sesquicarbonate could be transferred to the storage silo in approximately one hour versus two to four hours for sodium bicarbonate. In addition, sesquicarbonate operation did not require the use of the bin activator, whereas bicarbonate operation required both the use of the bin activator and frequently required hitting the silo discharge hopper and chute with a sledge.

The NO_x reduction additive injection systems also performed very well. The maximum flowrate through the ammonia system was found to be inadequate during early additive tests, so the piping system was revised to extract vapor from the ammonia tank as well as the liquid that went to the vaporizer. This revision worked very well for the short term tests.

The original dry additive design used a six ton dual storage bin above the K-Tron feeder for dispensing pulverized urea and ammonium bicarbonate. With this design, the additive discharge went to the downstream side of the pulverizers. Unfortunately, it was virtually impossible to discharge the pulverized additives out of the hoppers into the K-Tron due to severe agglomeration of the materials. Thus, 50-lb bags of prilled urea and granular ammonium bicarbonate were purchased. The bags were dumped directly into the K-Tron feeder, and since the material particle size was large, the feeder discharge hoses were repiped to upstream of the pulverizers. This modification worked extremely well and demonstrated that on a commercial application, grinding of the sodium and additive products together was practical and could reduce project costs.

ECONOMICS OF DRY SODIUM/ADDITIVE INJECTION

The estimated costs of installing dry sodium/additive injection on the 222-MW Nixon Unit No. 1 is shown in Table 2. The evaluation is based on cost factors developed by the Colorado Springs Department of Utilities for retrofitting Nixon 1 with dry sodium injection, if required in the future. The annual cost of additive injection for 25 ppm NO_x removal (50 ppm to 25 ppm; 50% NO_x removal) was calculated from the test data shown in Figures 13 and 14. It is estimated that on the Nixon application, the capital cost of the additive system, urea or ammonia, is approximately 7 percent of the total dry injection capital cost. For the sodium sesquicarbonate system, the annual additive cost is 7.5% to 12.1% of the annual sorbent cost and 4.5% to 7.1% of the total annual operating costs. For the sodium bicarbonate system, the annual additive cost is 5.0% to 8.6% of the annual sorbent cost and 3.4% to 5.7% of the total annual operating costs.

SUMMARY

This project demonstrated on a full scale utility boiler that the use of additives can successfully eliminate the brown plume problem associated with dry sodium injection. Specific conclusions from this project include the following:

- The SO₂ and NO_x removal data from Phase 2 with both sodium sesquicarbonate and sodium bicarbonate is clearly consistent with the past data from Phase 1 of the project.
- The NO_x emissions from dry sodium injection obtained during Phase 2 were similar to the data generated from Phase 1. The formation of a reddish-brown plume resulted at stack NO_x concentrations above 30 ppm (approximately). It should be emphasized that the visual threshold of NO_x from a power plant stack depends on a number of factors and thus would be site specific.
- An addition rate of approximately 3.5% (lb additive/lb sorbent) of either urea or ammonia reduced the NO_x from 50 ppm to 25 ppm (below the visual threshold).

Ammonium bicarbonate, however, was not very effective. A 3.5% additive injection rate resulted in only 10% NO₂ removal.

- All of the additives tested resulted in unreacted ammonia leaving the system and exiting the stack. It will be essential, on a commercial application, to optimize additive injection both to limit ammonia emissions and reduce additive costs.
- Tests on the fabric filter indicated that sorbent/additive injection resulted in no significant impact on outlet particulate emissions or increases in bag weights.
- For the R.D. Nixon application, the estimated cost of additive injection would increase the capital installation cost by approximately seven percent and the annual additive cost would range from approximately 5% to 12% of the annual sorbent cost.

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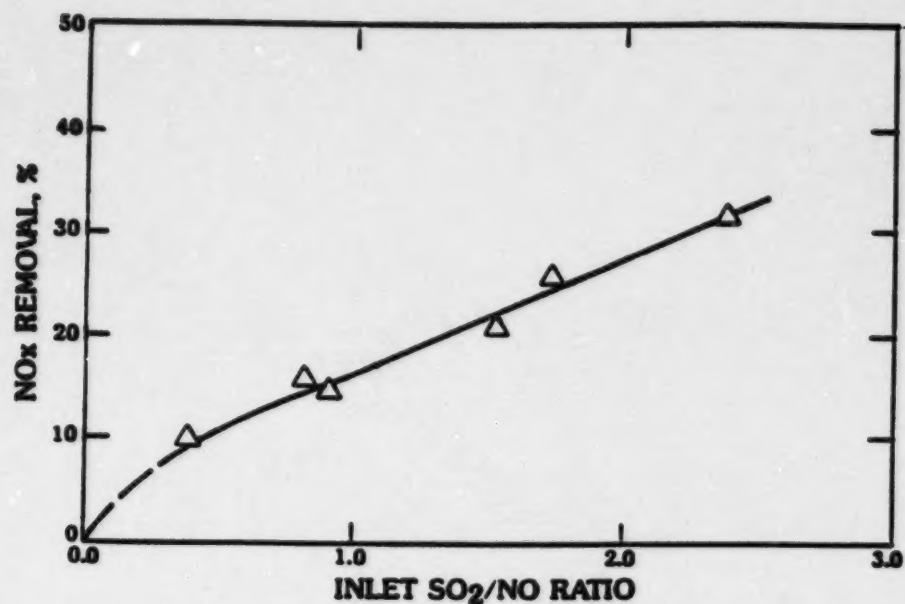


Figure 1. NO_x Removal Versus System Inlet SO₂/NO Ratio for Sodium Bicarbonate Injection. (Reference 4)

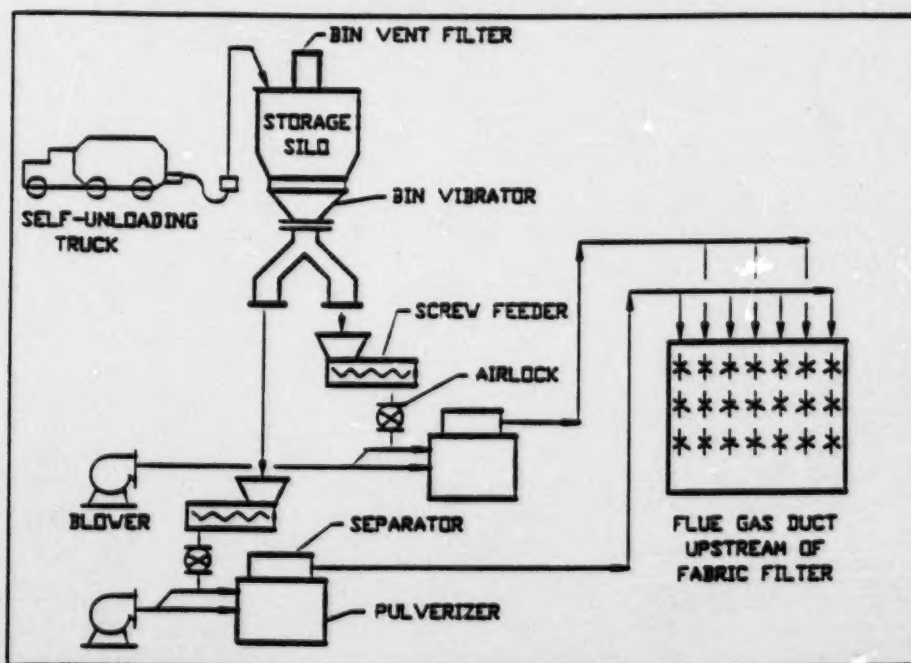


Figure 2. Schematic of Sodium Sesquicarbonate/Sodium Bicarbonate Storage, Feed, Pulverization, and Injection System.

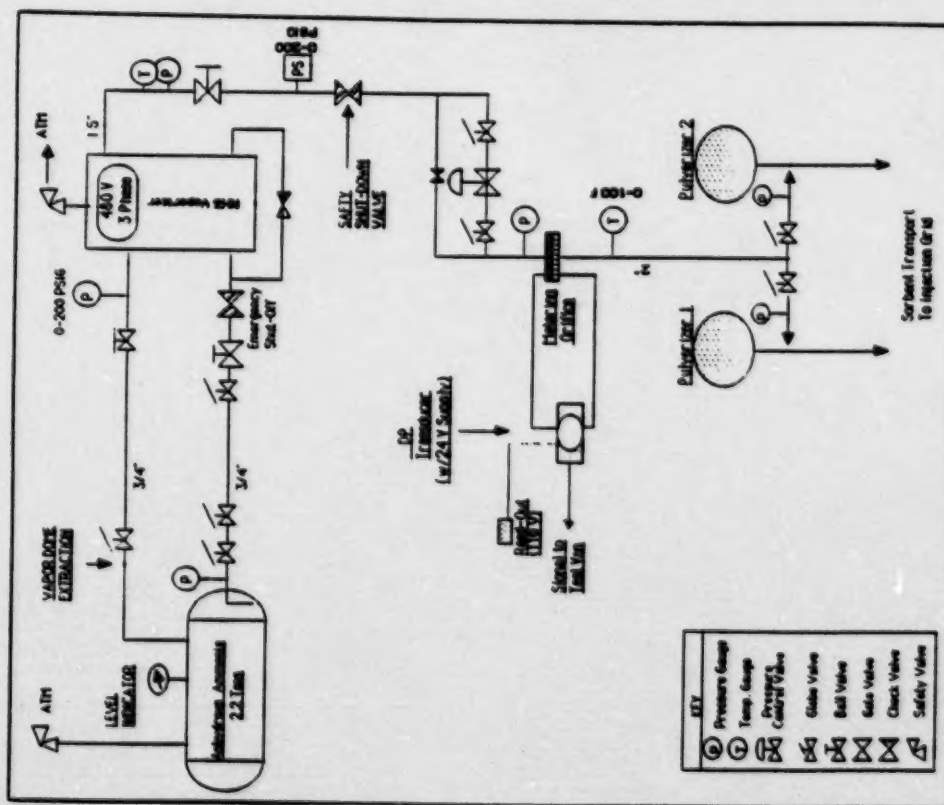


Figure 3. Schematic of Ammonia Additive Injection System.

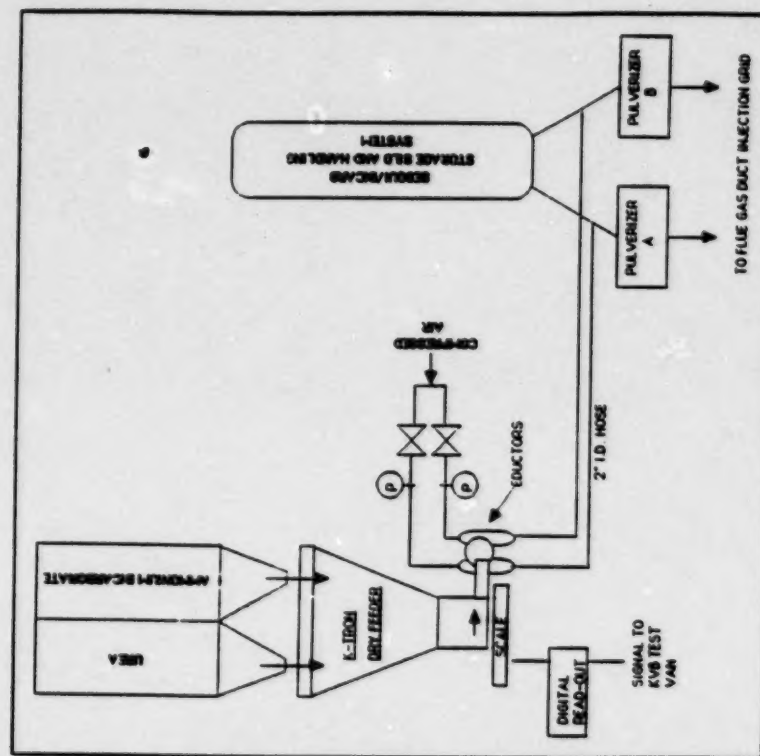


Figure 4. Schematic of Urea/Ammonium Bicarbonate Injection System.

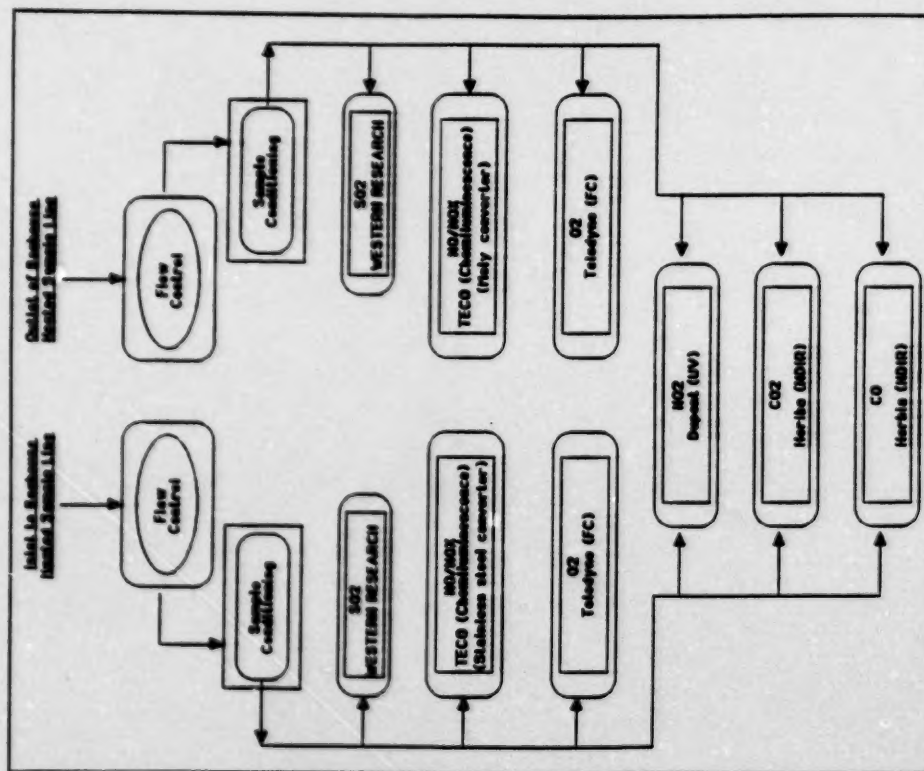


Figure 5. Schematic of Continuous Gas Monitoring System.

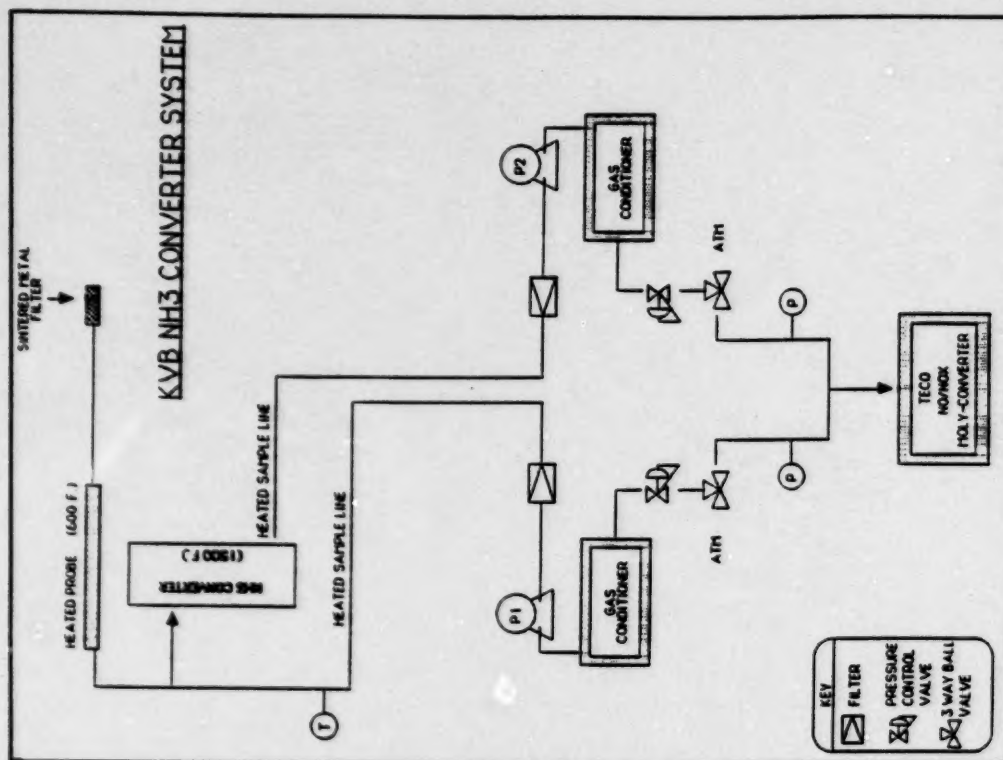


Figure 6. Schematic of Ammonia Gas Monitoring System.

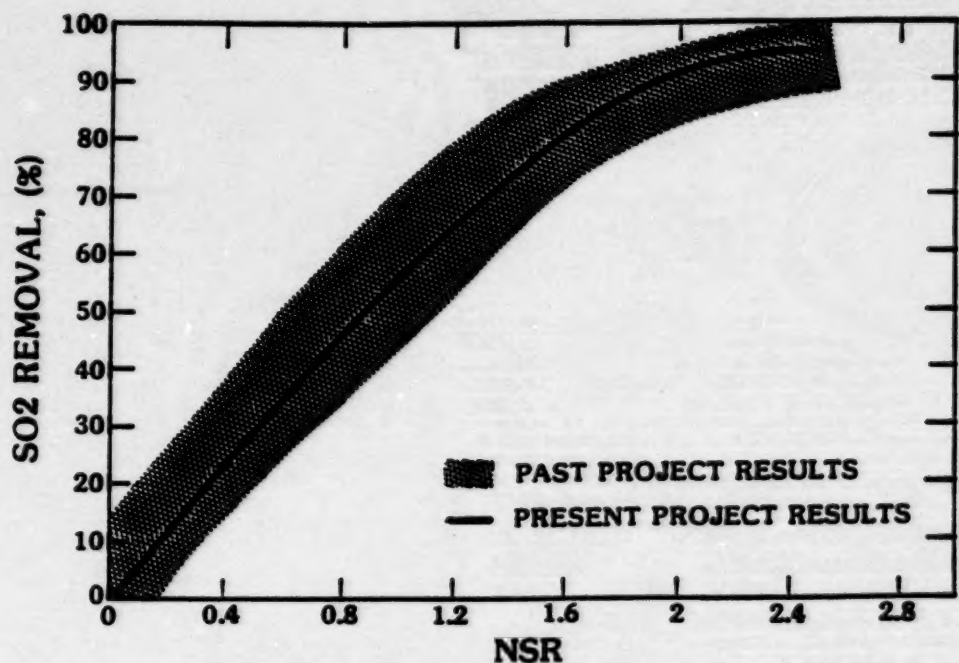


Figure 7. Comparison of Phase 1 and Phase 2 SO₂ Removal Versus NSR for Sodium Sesquicarbonate Injection.

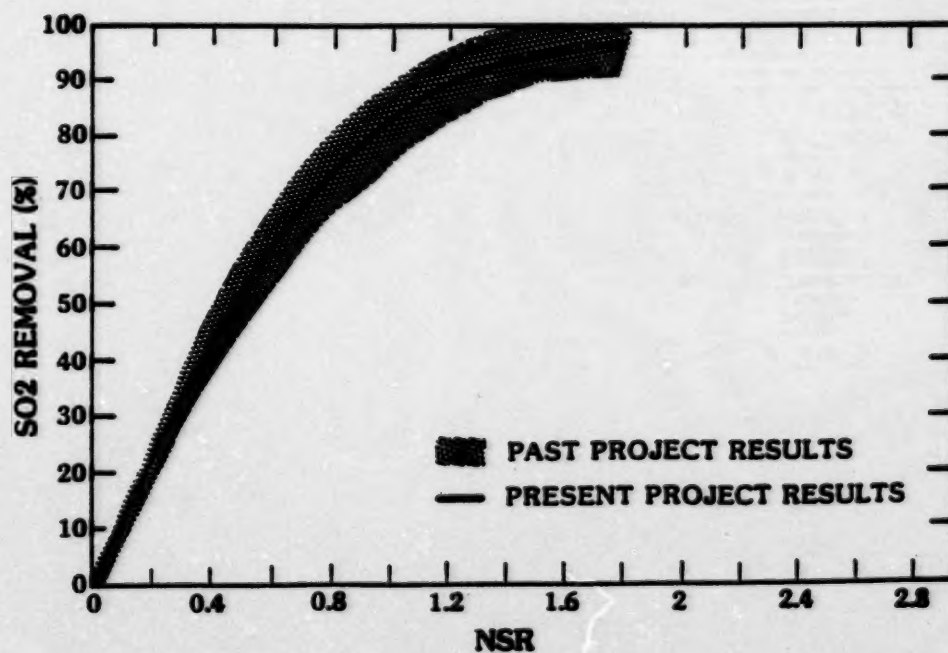


Figure 8. Comparison of Phase 1 and Phase 2 SO₂ Removal Versus NSR for Sodium Bicarbonate Injection.

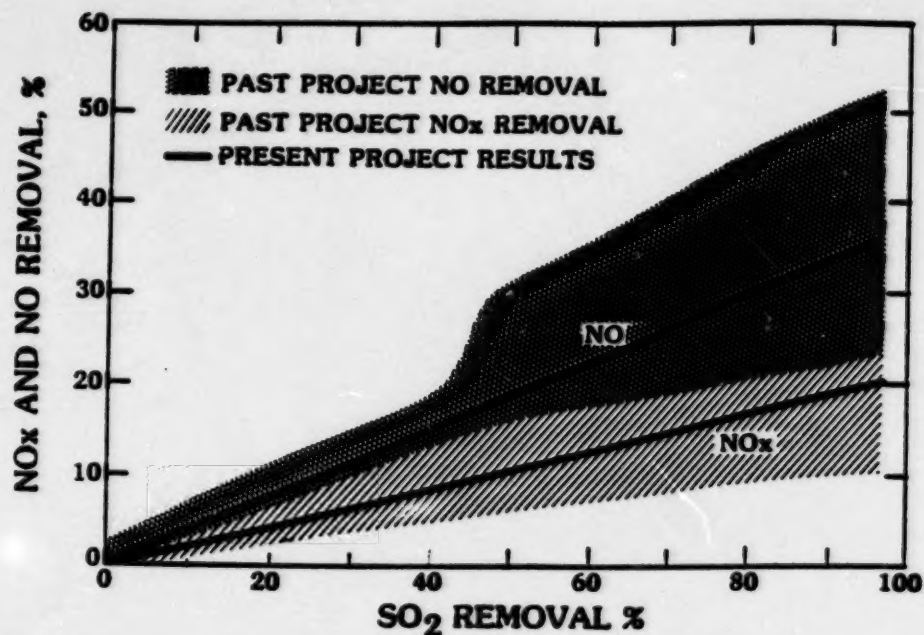


Figure 9. Comparison of Phase 1 and Phase 2 NO_x/NO Removal Versus SO₂ Removal for Sodium Sesquicarbonate Injection.

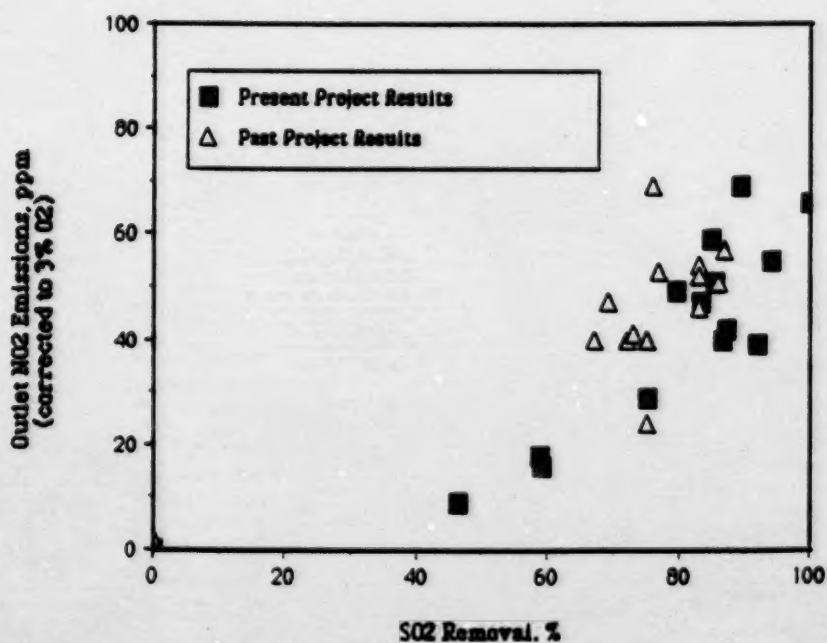


Figure 10. Comparison of Phase 1 and Phase 2 Outlet NO₂ Emissions Versus SO₂ Removal for Sodium Sesquicarbonate Injection.

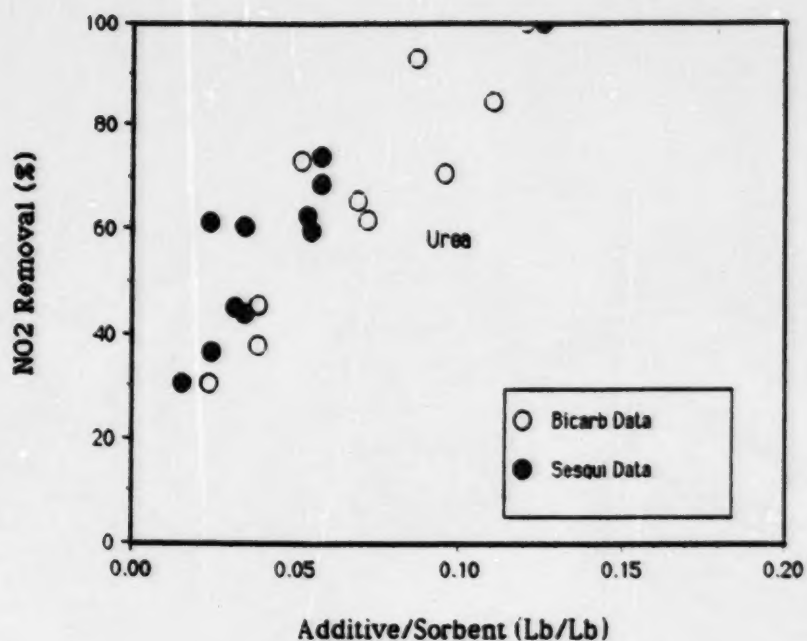


Figure 11. NO₂ Removal Versus Additive to Sorbent Mass Ratio for Urea.

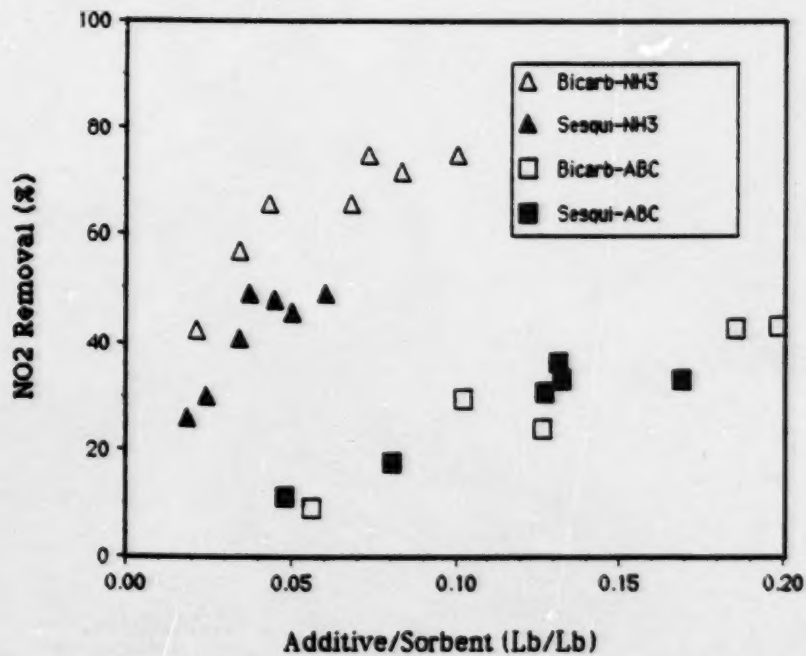


Figure 12. NO₂ Removal Versus Additive to Sorbent Mass Ratio for Ammonia and Ammonium Bicarbonate.

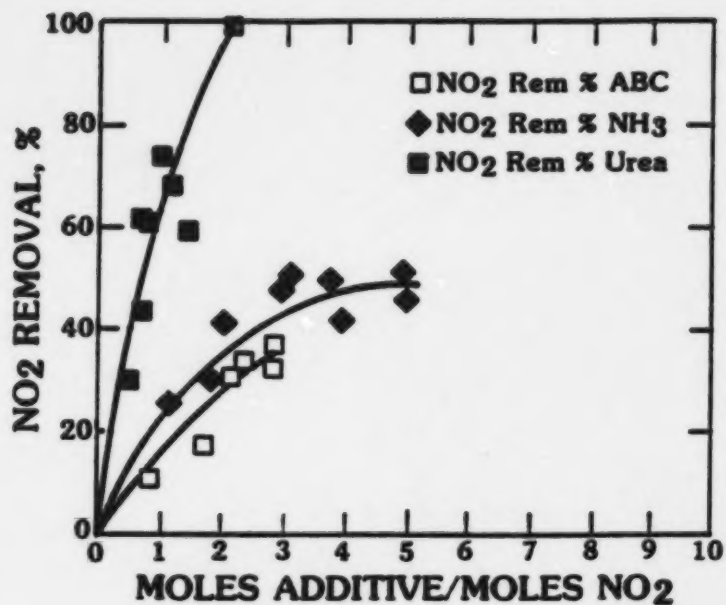


Figure 13. NO₂ Removal Versus Additive Injection Molar Ratio to Inlet NO₂ for Sodium Sesquicarbonate Injection.

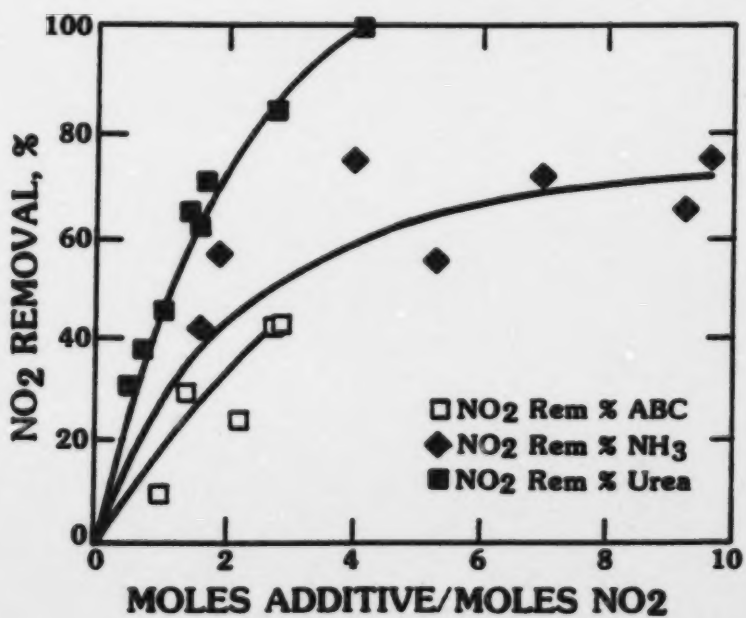


Figure 14. NO₂ Removal Versus Additive Injection Molar Ratio to Inlet NO₂ for Sodium Bicarbonate Injection.

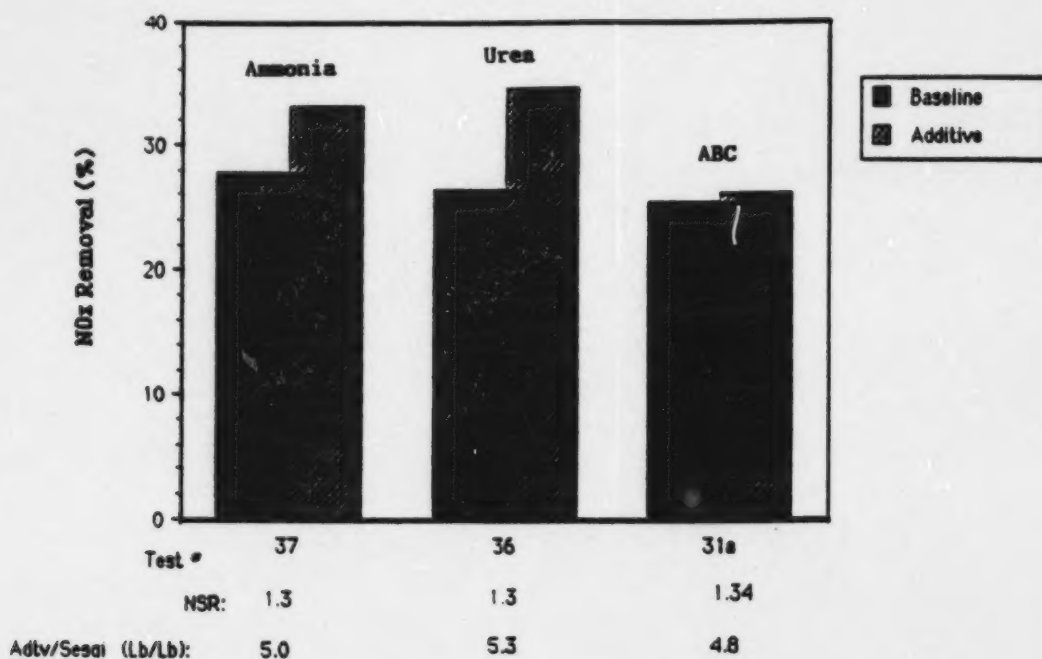


Figure 15. Effect of Ammonia, Urea, and Ammonium Bicarbonate Additive Injection on NO_x Removal.

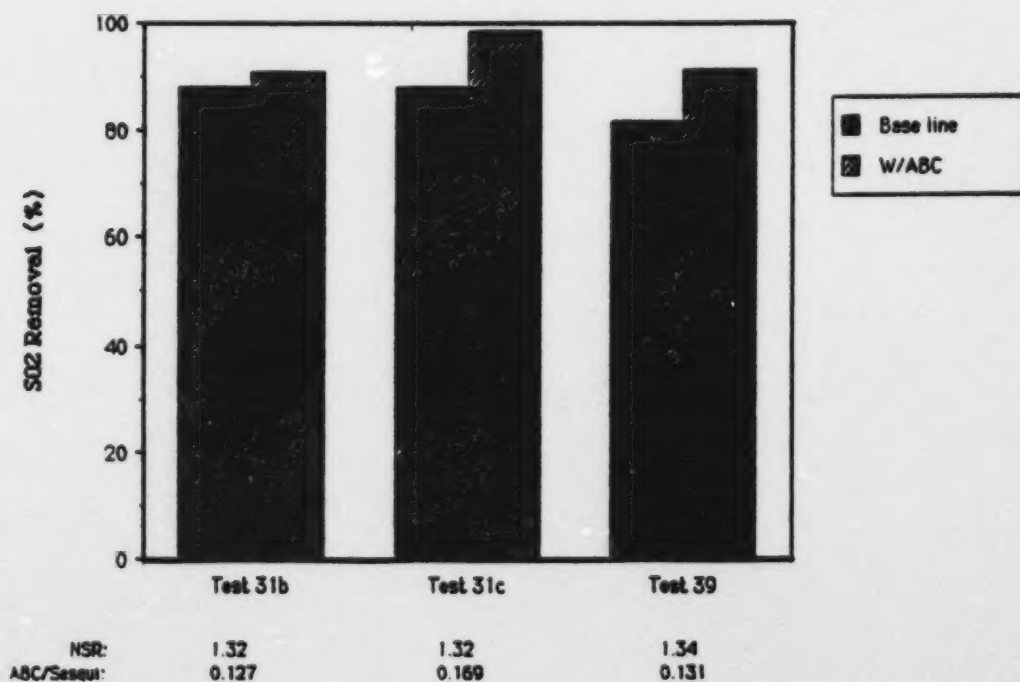


Figure 16. Effect of Ammonium Bicarbonate Additive Injection on SO₂ Removal.

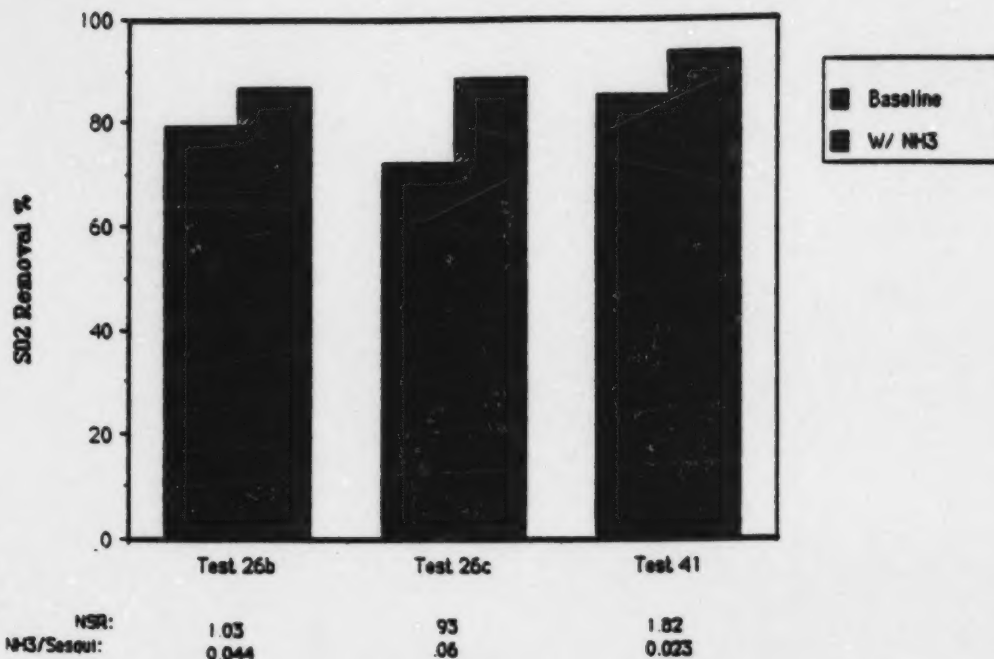


Figure 17. Effect of Ammonia Additive Injection on SO₂ Removal.

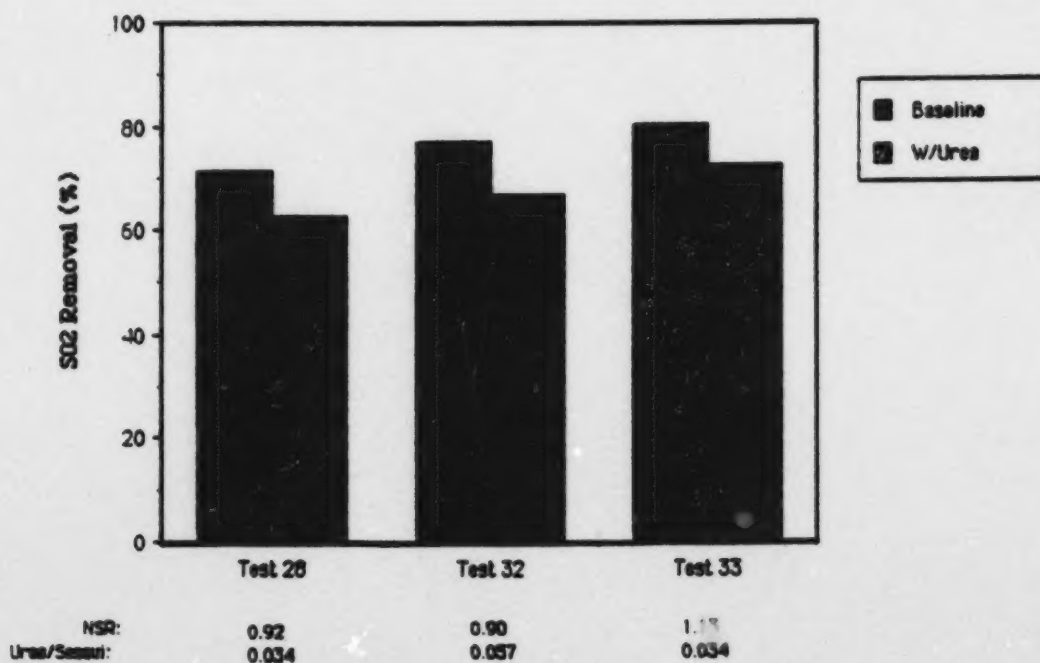


Figure 18. Effect of Urea Additive Injection on SO₂ Removal.

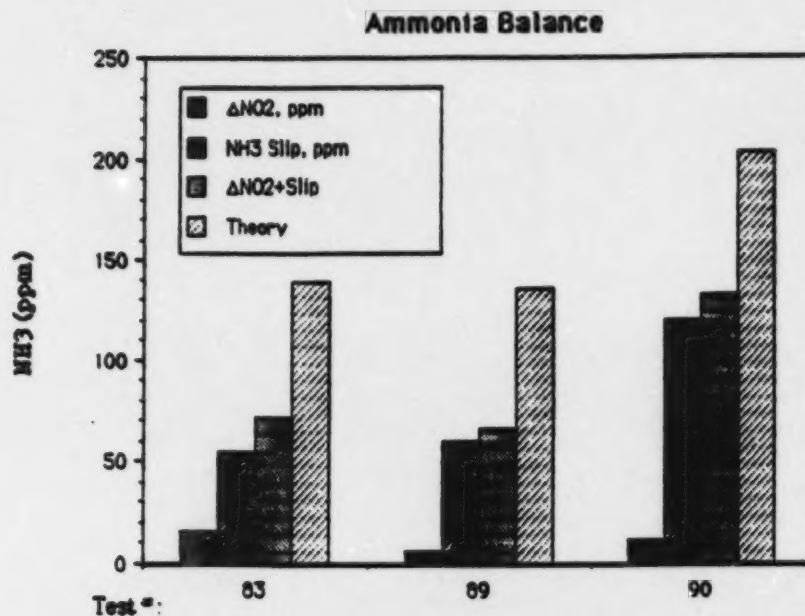


Figure 19. Ammonia Balance for Ammonia Additive Injection. NO_2 Capture, NH_3 Slip, and Theoretical Maximum NH_3 Concentration.

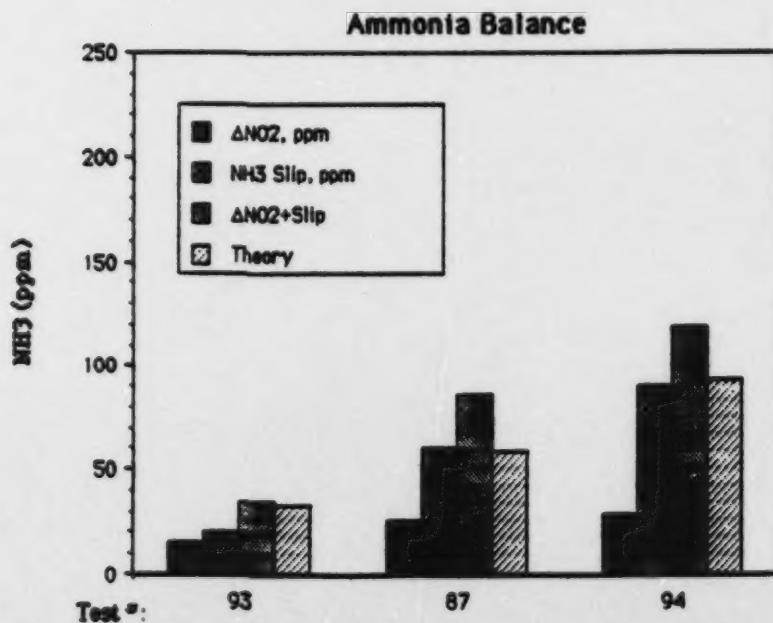


Figure 20. Ammonia Balance for Urea Additive Injection. NO_2 Capture, NH_3 Slip, and Theoretical Maximum NH_3 Concentration.

TABLE 1

COMPARISON OF COALS USED DURING TEST PROGRAM
Ultimate Analysis (As Received Basis)

	<u>Cyprus Yampa</u>	<u>Cyprus Empire</u>	<u>Arch Minerals</u>	<u>Colowyo</u>
% Moisture	9.17	13.07	13.64	15.79
% Carbon	64.18	59.95	60.86	61.40
% Hydrogen	4.36	4.20	3.88	3.74
% Nitrogen	1.45	1.08	1.10	1.20
% Sulfur	0.49	0.38	0.52	0.31
% Ash	8.24	8.62	6.87	5.07
% Oxygen (Δ)	12.11	12.70	13.13	12.49
Btu/lb (as recd)	11329	10502	10334	10649

TABLE 2

ESTIMATED COSTS OF INSTALLING DRY SODIUM INJECTION ON NIXON UNIT NO. 1
(1988 COST)

	Sodium Sesquicarbonate Injection System	Sodium Bicarbonate Injection System
1) Capital Cost	\$7,300,000	\$7,300,000
2) Fixed Operating Cost (\$/year)		
Operating Labor	\$ 295,000	\$ 295,000
Maintenance Labor	\$ 90,000	\$ 90,000
Administrative Labor	\$ 30,000	\$ 30,000
Maintenance Materials	\$ 200,000	\$ 200,000
Total Fixed Operating Cost	\$ 615,000	\$ 615,000
3) Variable Operating Cost (\$/year)		
Sodium Sorbent	\$1,525,000	\$2,200,000
Additive - Ammonia	\$ 185,000	\$ 110,000
Additive - Urea	\$ 115,000	\$ 190,000
Power	\$ 30,000	\$ 30,000
Waste Disposal	\$ 200,000	\$ 200,000
Fabric Filter Bag Replacement	\$ 65,000	\$ 65,000
Total VOC (with ammonia)	\$2,005,000	\$2,625,000
Total VOC (with urea)	\$1,935,000	\$2,705,000

Basis of Evaluation:

- 1) The evaluation is based on cost factors developed by Colorado Springs Department of Utilities for retrofitting the 222-MW Nixon Unit No. 1 with dry sodium injection if required in the future. The cost factors are based on the methodology presented in EPRI Report CS-4373 (8).
- 2) The design conditions are as follows:
 Flue Gas: 1,000,000 acfm; 300°F; 8% moisture; 350 ppm (wet) SO₂;
 Coal: Colorado coal; 100 tons/hr feed; 10,500 btu/lb; 0.5% sulfur
 Operation: 65% plant capacity factor
 Sodium Sesquicarbonate System: 70% SO₂ removal; 55% sodium utilization;
 5970 lb/hr feed at 100% plant load; 16,980 tons/year usage
 Sodium Bicarbonate System: 70% SO₂ removal; 90% sodium utilization;
 4080 lb/hr feed at 100% plant load; 11,630 tons/year usage
 Additive Injection System: 50 ppm to 25 ppm NO_x reduction (50% removal);
 urea feed: 185 lb/hr (520 tons/year) for sesqui. 305 lb/hr (870 tons/yr)
 for bicarb; ammonia feed: 345 lb/hr (980 tons/year) for sesqui, 205 lb/hr
 (590 tons/year) for bicarb
- 3) Capital Cost includes sorbent unloading (by rail) and bulk storage, sorbent and additive preparation (including pulverizers, feeders, day bins), injection piping/header system, process instrumentation and controls, and additive (ammonia or urea) feed system. The present fabric filter and ID fans do not require modification for dry sodium injection.
- 4) Sorbent/Additive Costs based on the following 1988 prices: sodium sesquicarbonate \$60/ton f.o.b. Green River, WY; sodium bicarbonate \$160/ton f.o.b. Green River, WY; freight from Green River to Colorado Springs \$30/ton; urea \$199/ton f.o.b. Cheyenne, WY; ammonia \$168/ton f.o.b. Cheyenne, WY; freight from Cheyenne to Colorado Springs \$20/ton. (References 9,10,11)
- 5) Power Costs based on 22.7 mills/kwh, 1-inch pressure drop increase across fabric filter for sodium bicarbonate injection, and no increase in pressure drop with sodium sesquicarbonate injection.
- 6) Waste Disposal Cost based on present on-site landfill with groundwater monitoring system.
- 7) Bag Replacement Cost is based on the cost of replacing the bags every four years versus the present eight year cycle at \$90 per bag.

DUCT INJECTION TECHNOLOGIES FOR SO₂ CONTROL

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Charles J. Drummond, U.S. Department of Energy
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Kenneth R. Murphy, General Electric Environmental Systems,
Joseph T. Newman, Bechtel National, Inc.,
Eric A. Samuel, General Electric Environmental Systems,
Robert M. Statnick, Consolidation Coal Company, and
Mark R. Stouffer, Consolidation Coal Company,

ABSTRACT

Research being conducted for the development of duct injection technology under the U.S. Department of Energy's Flue Gas Cleanup Program is discussed. Three completed proof-of-concept testing projects have demonstrated that duct injection technology is capable of reducing SO₂ emissions from pre-NSPS power plants by 50% to 70%. An analysis of the data collected over the last three years under these projects is presented. These projects also identified areas of technical concern that must be resolved by future research efforts. A description of plans for a comprehensive effort to bring this technology to a state of commercial readiness by 1992 is provided.

DUCT INJECTION TECHNOLOGIES FOR SO₂ CONTROL

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	<u>Page</u>
I. Introduction - Charles J. Drummond, U.S. Department of Energy	8-26
II. Results of Proof-of-Concept Tests	8-27
a. Hydrate Addition at Low Temperature (HALT) Process - Manyam Babu, Donald Kerivan, and K. Lee, Dravo Lime Company; and Dale A. Kanary, Ohio Edison	8-27
b. Confined Zone Dispersion (CZD) Process - Joseph T. Newman, Bechtel National, Inc.	8-30
c. In-Duct Scrubbing (IDS) Process - Kenneth R. Murphy, Eric A. Samuel, and Atef Demian, General Electric Environmental Systems	8-38
d. Humidification Scale-Up Using Multiple Nozzle Arrays - Mark R. Stouffer and Robert M. Statnick, Consolidation Coal Company	8-42
III. Future Research for the Development of Duct Injection Technology	8-45
a. Analysis of Research Goals - Charles J. Drummond, U.S. Department of Energy	8-45
b. Duct Configuration Survey Results - David S. Henzel, Burns and Roe Services Corporation	8-46
c. Description of DOE's Comprehensive Research Program - Charles J. Drummond, U.S. Department of Energy	8-48
IV. References	8-50
V. Figures and Tables	8-52

INTRODUCTION

The U.S. Department of Energy sponsors a Flue Gas Cleanup Program to develop environmental control technology for coal-fired utility boilers. The goal of the Flue Gas Cleanup Program is to promote the widespread use of coal by providing the technology necessary for its utilization in an environmentally and economically acceptable manner. To implement this program, research and development activities are occurring in a number of different areas. The area of activity that is described in this paper is SO_2 emissions control. The goal of this area of the Flue Gas Cleanup Program is to develop low-cost SO_2 emissions control technology that can be installed on existing coal-fired power plants if proposed acid rain legislation is enacted.

Current work in this program has concentrated on developing technologies suitable for retrofitting older plants that were built prior to the promulgation of New Source Performance Standards (NSPS) in 1971. These pre-NSPS utility boilers are the single largest remaining source of uncontrolled power-plant SO_2 emissions in the United States. Each plant in this population has its own particular site-specific performance and operating requirements, and is subject to a unique set of economic and environmental constraints. Presently proposed regulatory actions to reduce the SO_2 emissions of Eastern and Midwestern power plants could affect more than 200,000 MW(e) of power generating capacity.

The general goal of this SO_2 emissions control research effort is to provide simple, cost-effective technical options that can be applied to existing plants to satisfy possible future acid rain control regulations. Such processes should prove capable of a minimum of 50% removal of SO_2 at a cost of less than \$500/ton of SO_2 removed (compared to a baseline cost of \$1000/ton of SO_2 removed for wet scrubber technology). They should also be able to be installed in the limited space available at an existing plant. A wide number of alternatives are available for reducing SO_2 emissions from fossil-fuel power plants. The choices can be grouped according to where they are applied along the fuel path--before, during, or after combustion. Emphasis under the Flue Gas Cleanup Program has focused on in-duct sulfur capture, which involves the introduction of a calcium-based chemical reagent into the flue gas somewhere between the air preheater and the electrostatic precipitator (ESP). Duct injection, which falls into the category of post-combustion control, produces a non-hazardous waste in a dry solid form that can be disposed of in a convenient and safe manner. Because of its low capital cost, duct injection economics appear to be highly favorable relative to wet limestone slurry scrubbing.

Note also that duct injection technology satisfies the key criteria postulated in the Lewis-Davis joint U.S.-Canadian report on acid rain control: favorable cost-benefit ratio, application to a high number of sources of emissions, and the ability to be applied to high-sulfur coal. Most of the work funded to date has been at the proof-of-concept level, although some smaller scale support work is also being conducted. In 1985, three projects were begun to test duct injection technology using slipstreams from operating coal-fired power plants. The size of test units constructed at these plants ranged from three to five megawatts (electric). These tests were completed in 1988. The results of these tests, and a description of future research planned by the U.S. Department of Energy for the development of duct injection technology, are presented here.

RESULTS OF PROOF-OF-CONCEPT TESTS

HYDRATE ADDITION AT LOW TEMPERATURE (HALT) PROCESS

This section presents highlights of results obtained during operation of the 5 MWe HALT pilot unit at the Ohio Edison Company's Toronto power station. The HALT process involves injection of calcium hydrate particles into the flue gas stream prior to cooling the gas by humidification with a fine spray of water (1,2). A slipstream of flue gas from either of two operating 65 MWe boilers downstream of the air preheaters was ducted to the HALT unit. The HALT equipment was at grade and entirely in the open except for selected control equipment.

Gas Cooling By Humidification

For successful continuous operation of the process, mitigation of conditions causing duct wall wetting and solids deposition merit the highest attention. The plant cannot run continuously if the duct wall is wetted even slightly because the heavy loading of inlet solids causes duct solids accumulation and run interruption. Solids deposition can occur in the duct owing to any of the following reasons:

- o Incorrect selection of spray nozzles
- o Inappropriate nozzle layout and/or orientation
- o Incorrect operation of nozzles and/or poor maintenance
- o Low gas velocities
- o Eddy currents caused by physical obstructions to gas flow or duct discontinuity due to flanges, ports, or other openings
- o Spraying excessive quantities of water at one location
- o Routine dropout of dry fine solids, which can be reentrained by air lancing

Selection of appropriate nozzles and layout design is more crucial for a small test duct than for a commercial-sized duct application. It is extremely important to have a diagnostic device that will detect a potential wall-wetting condition and alert the operator. Two rings of thermocouples, surface mounted on the outer wall of the duct, were connected to a strip-chart recorder for continuous monitoring of duct wall conditions. The wall temperatures measured were an indication of the temperature of the gas flowing against it on the inside of the duct. Wall wetting was indicated by an isolated thermocouple reading differing from others at the same location indicating a temperature closer to the gas wet-bulb temperature.

The evaluation of several nozzle layout configurations and the collection of shielded gas temperature profile measurements were required at Toronto prior to determining the desired combination and number of nozzles, and resulted in a decision to use two-stage gas cooling. High inlet gas temperatures of 350°F to 380°F required the injection of excessive quantities of water, which could not be sprayed at one location. The small size of the ducting (31" x 31") and the need to maintain a minimum distance between the nozzles and the duct wall forced the nozzles to be confined to a small window inside the ducting. The temperature profile measurement in the ducting indicated poor radial mixing. Multiple smaller nozzles were indicated as opposed to fewer larger capacity nozzles. The difference in gas temperature spread in the duct cross section observed with 5 nozzles is much greater than when 8 nozzles are used. The effect of staged cooling with an auxiliary water injection location upstream of the main water spray is shown in Figure 1. The objective was to obtain and maintain sustained operation at an approach to saturation of 20°F or less. Using multiple Heat Systems 900-5 dual-fluid nozzles and two-stage gas cooling, the Toronto test unit was operated successfully 24 hours per day, seven days per week, for a period of eight weeks.

HALT Unit Performance

Commercial Longview hydrated lime was used during all of the tests conducted at Toronto. Hydrate utilization maximization is an important consideration because this would determine the primary viability of the process. Utilization was calculated by dividing the measured gas phase removal efficiency by the applied Ca/S stoichiometric ratio. The stoichiometric ratio calculations are based on inlet SO₂ loading and calcium hydroxide feed rates. All of the tests were confined to once-through solids injection. No solids recycle tests were conducted at Toronto.

Approach to the Adiabatic Saturation Temperature --

Approach temperature, in this process, is the single most important variable, followed by the Ca/S stoichiometric ratio (3,4). Because both of these factors are of major importance, data analysis can be simplified by comparing performance data in specific narrow ranges of Ca/S molar ratios. Each of the data points on the figures for hydrate utilization and removal efficiency (see Figures 2 and 3) represents a one-hour average of operation of the unit. The best regression fit for the data is the middle curved line indicated on the plot. The lines on either side of this line represent a 95% confidence limit for the data presented. The distance between the confidence lines depends on the sample variance and the sample size. At a 20°F approach to the adiabatic saturation temperature, another vertical limit line is drawn. This line indicates, with 95% confidence, that the limits an isolated experiment conducted at a 20°F approach will lie within the bounds. The larger the data scatter, the wider is this range, which is drawn at two times the standard deviation of the independent variable. Each set of data represents 8 to 10 days of plant operation. The variations in the runs reported were thought to be caused by differences in hydrate shipments received, swings in inlet SO₂ levels, and changes in the inlet gas temperature. Control of the Ca/S ratio was not automatic by design. The hydrate mass feed rate was manually set, with the flow varying from the set value by the response time of the Milltronics flow sensor and the speed controller on the screw feeder combined with the flow characteristics of the hydrate. The variation in the Ca/S molar ratio from the set value was also caused by fluctuations in gas flow rate, swings in inlet SO₂ level, and changes in the gas temperature. Manual operator intervention was required periodically to maintain the desired Ca/S ratio.

A review of the data provides the following conclusions:

- o Hydrate utilization is highly dependent on approach temperature. Operation at as low an approach temperature as possible within system limits is indicated.
- o Performance differences between various hydrate shipments seems to be reduced at low approach temperatures.
- o Low approach temperatures seem to reduce the difference in performance at different Ca/S ratios.

The data are presented in a different format at the discrete approach temperatures of 20°F and 30°F for various Ca/S molar ratios (using data disks 20, 21, 22, and 26) in Figure 4.

- o At a Ca/S molar ratio of 1.74 and a 20°F approach temperature, all of the runs (regardless of hydrate quality) have nearly the same utilization.

- o Variation of sorbent utilization with Ca/S molar ratio is more pronounced at a 30°F approach temperature than at a 20°F approach temperature.
- o Effect of hydrate quality is a more important factor at higher approach temperatures.

Approach to the adiabatic saturation temperature, in this context, can be considered to be a measure of the time it takes for the gas to reach a given dryness. As long as moisture and hydrate co-exist in the gas the hydrate continues to react with SO₂. Low approach temperatures make the attributes of the sorbent less important. Increasing the solids residence time in the humidification section by solids recycle is strongly indicated.

Lime Hydrate Stoichiometry --

Tests at Toronto were designed to be conducted at a Ca/S molar ratio of 2.0 with selected tests conducted at a Ca/S molar ratio around 1.5. The Ca/S molar ratio was calculated based on the measured inlet SO₂ loading and the hydrate feed rate. A review of the data shows an expected performance trend where hydrate utilization is highest at the lowest Ca/S ratio. For a given removal efficiency there is an optimum Ca/S ratio. SO₂ removal efficiency was observed to be 52.9% at an average Ca/S molar ratio of 2.05 and a 20°F approach to the adiabatic saturation temperature.

If the SO₂ removal efficiency required is 50%, the optimum Ca/S molar ratio is close to 1.74 at a 20°F approach temperature. If a higher SO₂ removal efficiency is required, a Ca/S ratio of 2.05 should be considered. Hydrate utilization is reduced by operation at higher approach temperatures by approximately 1.7% for every 10°F higher than a 20°F approach temperature.

Inlet Flue Gas Temperature --

High inlet flue gas temperatures and continual temperature fluctuations experienced over short periods of time were causes for concern at Toronto. As discussed earlier the quantity of water that had to be sprayed to cool the gas down from 300°F to 150°F dictated staging the sprays. It was observed that higher inlet temperatures result in better sorbent utilization.

Inlet SO₂ Concentration --

It was also observed that higher inlet SO₂ levels favor better hydrate utilization. Combining the temperature and inlet SO₂ dependence effects, it should be noted that favorable utilization is indicated when high S coal is burned at low excess O₂ levels (consistent with high utility plant demand) resulting in high gas temperatures.

Hydrate Quality --

The hydrate has a mean particle size of 5.6 microns. The mean B.E.T. particle surface area is fairly consistent varying from 15 to 26.5 m²/g. Attempts to relate hydrate particle physical attributes to process performance were inconclusive because of the limitations of the particle size measurement device for particles smaller than 2.0 microns and an inability to maintain all of the process conditions at constant values (viz., inlet gas temperature and SO₂ level).

Baghouse/ESP Hydrate Utilization --

The Toronto pilot plant was designed to remove particulates from the flue gas using a single compartment pulse jet baghouse. During a portion of the tests a rented Wheelabrator mobile ESP test unit was used in parallel with the baghouse. The ESP related tests were designed and conducted by the Southern Research Institute of Alabama.

A comparison of solids collected in the baghouse and ESP hoppers shows essentially no difference in hydrate utilization for the two different particulate collection devices studied. Samples were collected simultaneously from these two units. Two major qualifications apply to these results:

- a. The hydrate was injected downstream of the humidification water resulting in lower utilizations than upstream injection during these tests. This correction would apply to both units.
- b. The temperature drop across the ESP was, on an average, 80°F greater than the temperature drop across the baghouse (which was negligible). As references to the approach to the adiabatic saturation temperature in all of this work are for temperatures upstream of the collection device, a correction of the ESP data for this temperature drop would be necessary to allow comparison with the baghouse data. Based on this reasoning, the data suggests that baghouse performance should be marginally better than ESP performance.

Solids Leachate Analysis --

Analysis of leachate collected from HALT solids samples was conducted. The data from this analysis is reported in Table 1. In all cases the HALT solids meet RCRA limits for classification as a non-hazardous waste.

Conceptual Scaleup Design and Costs

Conceptual designs for the installation of the process on two existing coal-fired units (180 MWe and 500 MWe) and a detailed cost estimate have been completed. The cost analysis assumed solids recycle and the conceptual designs were based on a 2.5% S, 8.2% ash coal and a 65% SO₂ removal target. A summary of the first year costs is presented in Table 2.

Capital investment cost, as expected, is low. Cost of the sorbent is a major contributor to the variable operating costs accounting for about 45% to 50% of the total first year cost.

CONFINED ZONE DISPERSION (CZD) PROCESS

Process Description

The Bechtel Confined Zone Dispersion (CZD) process captures SO₂ by spraying a finely atomized slurry of hydrated lime into the ductwork of a utility boiler. The spray is injected between the air heater and the electrostatic precipitator (ESP), where the gas is typically at 280°F to 300°F. A sufficient run of straight duct is needed downstream of the point of injection to allow the slurry droplets to dry before they strike the duct walls or turning vanes at a bend. By using narrow angle sprays and carefully positioned atomizers, it is possible to obtain a wet zone in the middle of the duct with an envelope of hot gas between the wet zone and the duct walls. This is the principle of the confined zone.

Reagents --

Two reactive types of lime were used for these tests. One was a pressure hydrated dolomitic lime and the other a calcitic lime, obtained from a nearby power plant as a freshly slaked slurry. Commercial calcitic lime, obtained as a dry hydrate and mixed on site with water, was also tested but was not as reactive as the other two types. Fine grit was removed from the slurries before they were injected into the duct.

Atomization --

Two-fluid nozzles, with compressed air as the driving fluid, were used to atomize the lime slurry into the fine sprays needed to achieve rapid drying and reaction. These nozzles are particularly well suited for this application.

Pilot Scale Tests

The initial proof-of-concept tests were carried out on a 5-MWe scale at the J. H. Campbell Station of Consumers Power Company, where the test facility used a slip-stream of flue gas from Unit 1. Campbell Unit 1 is rated at 260 MWe and is normally base loaded. During the test period, the unit burned washed coal (averaging 11.3 percent ash and 2.2 percent sulfur) from the Peabody Coal Company's Sunnyhill Mine in Ohio.

Test Facility --

The pilot-scale test facility was designed to have a finely atomized spray of lime slurry injected into a stream of flue gas flowing through a straight run of cylindrical duct 3 feet in diameter and about 130 feet long. The entire test duct was insulated to minimize heat loss. The test duct tied into the ductwork of Unit 1 just upstream of the first-stage ESP, so flue gas carried entrained fly ash (5).

All of the gas passed through a small ESP directly downstream of the test section. This ESP had two fields in series and two hoppers. At a nominal flue gas flow rate of 21,000 acfm, the specific collection area (SCA) of the ESP was 165 square feet per 1000 acfm, the average gas velocity past the plates was approximately 3 ft/sec, and the plate spacing was 12 inches. Lodge Cottrell supplied the unit.

Test Program --

An 8-1/2 month test program began in October 1986 consisting of a 3-month shake-down period, 4 months of parametric tests, and a 6-week long duration test. During the duration test, the system operated 24 hours per day. Four weeks of this test were used to evaluate ESP performance.

Parametric Tests -- These tests systematically examined many of the variables that affect the process. The following parameters were varied:

- o Lime feed ratio: 0.5 to 3.0
- o Lime slurry concentration: 8 to 22 percent (by weight)
- o Downstream gas temperature: 180°F to 140°F
- o Gas velocity: 20 to 60 ft/sec measured upstream of the sprays
- o Atomizer design: Fourteen different atomizers and atomizer configurations were tried

- o **Lime:** Five different limes, both calcitic and dolomitic, were tested

The temperature of the incoming gas, and the concentrations of SO_2 and NO_x in the incoming gas could not be controlled. The gas inlet temperature varied from 270°F to 330°F. The gas inlet SO_2 concentration varied from 1190 to 1560 ppmv, wet basis. The gas inlet NO_x concentration, based on several measurements conducted on one day, was approximately 300 ppmv, wet basis.

An important objective of exploring a range of operating conditions was to develop techniques to avoid deposit buildup on the walls of the duct from the impingement of wet droplets.

Each parametric test generally lasted 3 to 4 hours, after which the inside of the duct was inspected to determine whether and how much deposition had occurred.

Duration Tests -- After the parametric tests had determined conditions that achieved at least 50 percent SO_2 removal and that avoided undue deposition inside the duct, the system was operated continuously for longer periods. These tests normally lasted about 20 hours, and one continued for over 40 hours.

ESP Test -- For 4 weeks during the duration tests, the concentration of particulates was measured upstream and downstream of the ESP to determine its removal efficiency. These measurements were made over a range of gas flows, gas temperatures, and lime injection rates. As a basis of comparison, the removal efficiency was also measured when no lime was injected. An on-line opacity meter downstream of the ESP continuously monitored its performance.

Particulate concentrations around the ESP were also measured during the shakedown period to establish that the unit operated satisfactorily. These measurements were made both with and without lime injection.

Summary of Results --

SO_2 Removal -- Total system (ductwork plus ESP) removals of SO_2 in excess of 50 percent were achieved using either pressure hydrated dolomitic lime or calcitic lime. The ESP removed an average of 7 percent of the SO_2 entering it. At the conditions tested, the calcitic lime required a somewhat lower lime feed ratio to remove 50 percent of the SO_2 than the pressure hydrated dolomitic lime did. This result was unexpected. Preliminary pilot-scale tests by Bechtel have indicated that pressure hydrated dolomitic lime was more effective. Possibly the improved performance of the calcitic lime resulted from the relatively long residence time (3+ seconds) in the spray zone during the Campbell tests.

Lime Utilization -- Lime utilization is defined as the percentage of lime fed that reacts with SO_2 . With pressure hydrated dolomitic lime injection, lime utilization ranged from 12 to 45 percent. With calcitic lime injection, lime utilization ranged from 26 to 60 percent.

NO_x Removal -- Preliminary tests with gas tubes showed moderate NO_x removals. However, subsequent tests with a chemiluminescent analyzer showed negligible removal.

Effect of Temperature -- Decreasing the gas temperature by injecting moisture (either as slurry or water) increases SO₂ removal. However, because lower temperature reduces the drying rate, it also increases deposition of solids in the duct. Temperatures between 150°F and 170°F (from 25°F to 45°F above the adiabatic saturation temperature of 125°F) were a practical compromise between the two opposing effects.

Control of Deposition -- The small diameter test duct presented special problems in minimizing deposits. Spray geometry, alignment, and degree of atomization were all extremely important. With a given spray nozzle, the liquid flow to the nozzle had to be limited to prevent wet droplets from impinging on the duct walls. Limiting the injection of liquid resulted in also limiting the flow of gas, since the best removal efficiencies were obtained at final gas temperatures of about 160°F. As a result, for prolonged operation with minimal deposition, the gas flow was limited to 30 ft/sec as measured upstream of the spray nozzles, and the slurry was injected through two nozzles 40 ft apart along the duct. Note that this restriction on flue gas flow appears to apply only to this small test duct where the spray nozzles are located only 18 inches away from the duct walls.

ESP Performance -- When lime was injected into the gas, the resulting lower temperature and higher moisture content were expected to offset the higher concentration of particulate matter entering the ESP. Consequently, emissions were expected to remain about the same as they were before lime injection. This was the case when ESP performance was briefly investigated during the shakedown period. However, detailed ESP tests conducted during the duration tests showed that particulate matter containing lime was harder to collect and thus emissions from the ESP increased when lime was injected. This result is contrary to the experience of others with ESPs located downstream from lime spray dry FGD systems. Analysis of the ESP results did not conclusively identify the reasons ESP performance fell off with lime injection. Electrical leakage from incompletely dried solids, uneven gas distribution because of ductwork bends near the ESP inlet, and particulate reentrainment inside the ESP are likely causes of the reduced performance.

Waste Products -- The waste products were a mixture of fine coal ash, reaction products consisting of sulfates and sulfites of calcium and magnesium, and unreacted lime. The waste is a fine, dry, free-flowing powder. No problems were encountered in discharging the material from the ESP hoppers. The waste also absorbed water readily and did not set up or solidify when moistened.

Process Control -- The test system was easy to stop, start, and control. Sophisticated sensors were not needed.

Corrosion -- No undue corrosion took place in the flue gas duct downstream of the injected lime slurry or in the ESP.

Large-Scale Tests

Large-scale tests were carried out at the Seward Station of Pennsylvania Electric Company (PENELEC). The CZD system was retrofitted onto one of two parallel flue gas ducts on the 140 MWe Unit 15. During the test period, the unit burned a 1.2 percent sulfur coal, the load typically varied from 135 MWe to 145 MWe, and the gas inlet temperature typically varied from 280°F to 300°F.

Test Facility --

The flue gas was treated in approximately 35 feet of (8 x 11 feet) straight ductwork section between two sets of turning vanes. The ductwork section and turning vanes were located between two existing ESPs. At a nominal flue gas velocity of 64 ft/sec, the duct section has only about a half-second residence time. After slurry injection, the dried reaction products and fly ash were collected in the second existing ESP (5).

Test Program --

A 5-month test program began in June 1987 consisting of 2 months of shakedown testing, 2 months of parametric testing with lime slurry, and 1 month of testing during continuous operation at 24 hours/day, 7 days/week. The tests were predominantly conducted with pressure hydrated dolomitic lime, but a limited number of tests with hydrated and freshly slaked calcitic lime were also run. During the test program, the inlet gas SO₂ and NO_x concentrations in ppmv, wet basis, varied from 730 to 870, and 360 to 470, respectively.

Parametric Lime Injection Tests -- These tests investigated the effects of lime concentration on the following:

- o Extent of flue gas desulfurization
- o Lime utilization
- o Maximum lime injection rate

Continuous Lime Injection Tests -- The system was operated continuously to determine the long-term effects of lime injection on the atomizers, duct deposits, and ESP performance.

ESP Tests -- Particulate removal efficiency testing of the ESP, with and without lime slurry injection, was conducted to determine the capability of the ESP to handle the additional grain loading when lime is injected into the system. An on-line opacity monitor mounted in the stack was also used to determine ESP performance during the testing.

Summary of Results --

Lime Injection Tests -- The lime injection tests confirmed that fine atomization and restricted lime feed rates were necessary to dry the atomized droplets sufficiently to avoid deposition on the turning vanes located about 35 feet downstream of the nozzles. The restricted feed rates limited the maximum SO₂ removal. The following results were obtained:

- o Temperature profiles taken in the duct cross section at several distances from the injection point confirmed that a true confined zone, a moist interior surrounded by hot gas, could be obtained.
- o With pressure hydrated dolomitic lime injection, SO₂ removal ranged from 6 to 30 percent depending on the slurry flow rate and concentration. The lime feed ratio ranged from 0.11 to 1.34. NO_x removal ranged from 8 to 21 percent and increased with increasing slurry concentration. Lime utilization, based

on combined SO_2 and NO_x removal, ranged from 23 to 90 percent. Lime utilization decreased with increasing slurry concentration.

- o With calcitic lime, either freshly slaked or a slurry prepared from dry hydrate, SO_2 removal, NO_x removal, and lime utilization were significantly lower than corresponding values for pressure hydrated dolomitic lime. The unexpected lower performance for the freshly slaked lime may have been caused by eroded nozzle tips. Time was not available to repeat the test with erosion-resistant tips.
- o It appeared that duct deposits could be prevented by limiting injection rates to the point where the atomized droplets dried before they reached the first interior duct surface, the turning vanes. However, because this was a manually controlled operation, it was not possible to follow load closely, particularly at night. Consequently, there were times when the injection rate was excessive, resulting in low downstream temperatures with some deposition on the vanes and surrounding areas. Poor atomization resulting from eroded atomizers also caused some deposits.

ESP Performance -- During short-term parametric tests, the opacity decreased and remained lower during lime injection and then increased when injection was stopped. During long-term continuous injection tests with either pressure hydrated dolomitic lime or calcitic lime, the opacity decreased at the start of injection and remained low. However, after 5 to 10 hours of operation the opacity increased and exceeded the original level before the start of injection. Off-power rapping was successful in restoring opacity to acceptable levels but was required intermittently.

Particulate removal efficiency tests were performed for fly ash alone (no injection), during injection of pressure hydrated dolomitic lime, and during calcitic lime injection. Only one slurry injection rate per test was evaluated. The average removal efficiency was slightly higher during calcitic lime injection and slightly lower during pressure hydrated dolomitic lime injection compared with fly ash alone. The average emissions were the same during calcitic lime injection but higher during pressure hydrated dolomitic lime injection compared with fly ash alone.

It should be noted that CZD testing was conducted with the ESP in an as-found condition. No attempt was made to optimize the mechanical and electrical condition prior to testing. Analysis of the ESP operating characteristics during the testing suggests that the ESP had some deficiencies with the automatic voltage controllers and rapping systems. In the future, PENELEC plans to install new systems for automatic voltage control, automatic rapping control, and discharge wire rapping.

Since the condition of the ESP was not optimum, its performance during the CZD tests should be regarded as preliminary. More testing is required to better assess the effect of the CZD process on ESP performance. These additional tests should be performed with the following:

- o A fine-tuned ESP

- o Longer periods of ESP conditioning time with injection
- o A plan to obtain comprehensive ESP operational data

Analysis of SO₂ Removal Data

The widely different test conditions at Campbell and Seward made it difficult to analyze the data on a common basis. Compared with Campbell, Seward had these principal differences:

- o Extremely short residence time
- o Much larger duct cross section
- o Higher gas velocity and gas flow rate
- o Finer and more uniform atomization
- o Higher total injection rates
- o Lower inlet SO₂ concentration
- o Lower SO₂ removals
- o High approach-to-saturation temperatures
- o Capability to establish a confined zone
- o Minimal duct deposits

Conditions at both sites served to limit the volume of slurry that could be injected. At Campbell, impingement of undried slurry droplets on the duct walls limited injection. At Seward, the need for slurry to dry before contacting the turning vanes only 35 feet downstream of the nozzles placed a more severe limit on the injection rate. A full-scale commercial system with a longer run of straight duct would not be limited in this way.

Correlation Approach --

Several rational and empirical approaches were investigated to correlate the data sets from the two test sites. Most of the approaches provided good correlations for data from either site, but they were not adequate to correlate the combined data set from both sites, and the correlation obtained would not extrapolate with any confidence. One approach did successfully correlate the combined data set and appears to provide reasonable extrapolations. This approach had three major characteristics:

- o The injection rates and gas flows for the two systems were normalized to make them directly comparable.
- o Significant measured variables were included directly in the correlation formula.
- o A coefficient, K, was added to the correlation formula to account for the effect of unmeasured variables, system differences, and lime type.

The injection rates and gas flows were normalized by dividing the water portion of the slurry feed rate in gallons per minute (gpm) by the gas flow rate in thousand standard cubic feet per minute (kscfm). This quantity was called the normalized water injection rate (NWIR). Other measured variables used in the correlation formula were feed solids in weight percent (WT %), the arithmetic average of the inlet and outlet SO₂ concentration in wet parts per million by volume (Avg SO₂), and approach to saturation temperature in °F (AST).

The form of the correlation equation chosen was

$$\text{Fraction SO}_2 \text{ removal} = K (\text{NWIR})^a (\text{Wt } \%)^b (\text{Avg SO}_2)^c (\text{AST})^d$$

Correlation Results --

The fully regressed correlation for three separate data sets gave the following values for the exponents, K, and R^2 :

Data Set	a	b	c	d	K	R^2
Seward pressure hydrated dolomitic lime	0.707	0.620	-0.208	+0.144	0.49	0.906
Campbell pressure hydrated dolomitic lime	0.806	0.278	-0.580	-0.675	346	0.830
Campbell calcitic lime	1.196	0.639	-0.210	-0.306	5.7	0.713

These results show a good fit for the Seward pressure hydrated dolomitic lime data, and somewhat poorer fits for the Campbell data. The values for the exponents and the coefficients are so widely different for the different data sets that a comparison of these values is not useful.

Further regression analyses examined the sensitivity of the fit to exponent values. A final regression produced the following results:

Data Set	a	b	c	d	K	R^2
Seward pressure hydrated dolomitic lime	0.65	0.45	-0.4	-0.4	27.3	0.877
Campbell pressure hydrated dolomitic lime	0.65	0.45	-0.4	-0.4	19.1	0.774
Campbell calcitic lime	0.65	0.45	-0.4	-0.4	24.4	0.654

Here, the exponent values are the same for each data set, and the fit of each set, as measured by R^2 , is only slightly worse than it was for the fully regressed results above.

A comparison of calculated versus actual SO_2 removal for the Seward and Campbell pressure hydrated dolomitic lime for the fully regressed correlations and the fixed exponent correlations is provided in Figure 5.

The range of the variables used in this correlation is as follows:

<u>Variable</u>	<u>Seward</u>	<u>Campbell</u>
NWIR, gal/kscf	0.06 - 0.15	0.2 - 0.36
Wt %	1.6 - 16	7.5 - 21
Avg SO ₂ , ppmv, wet basis	600 - 780	800 - 1200
AST, °F	95 - 130	25 - 55

The correlation provides reasonably accurate predictions of SO₂ removal when the variables are within these ranges. However, the accuracy of extrapolations outside these ranges is unknown, and they should be performed with caution.

IN-DUCT SCRUBBING (IDS) PROCESS

In-duct scrubbing is accomplished by injecting a slaked lime slurry with a rotary atomizer directly into existing ductwork thus eliminating the reaction vessel typical to wet and dry flue gas desulfurization technologies. As a result, matching the slurry drying process and the desired SO₂ removal to available duct residence time is a key to attaining efficiency goals. Collection of the reaction products along with fly ash is compatible with existing electrostatic precipitators. The lower volume of treated flue gas coupled with particulate resistivity beneficiation (due to added moisture) offsets increased mass loading.

In the IDS process, chemical reactions occur between the sulfur oxides present in the flue gas and the alkaline slurry droplets created by a rotary atomizer while evaporation is reducing the reaction products to a dry suspended particulate (6). The waste product is similar to that produced by conventional dry FGD systems, which is usually landfilled but can also be pelletized and used in the construction industry.

SO₂ absorption occurs in three areas in the IDS process: (1) the slurry injection zone, (2) the evaporation zone, and (3) the drift zone (7). Minor modifications to existing ductwork are required to physically support the vertically mounted atomizer and to enhance the gas/slurry mixing dynamics. Scaled cold flow model studies and two-phase, three-dimensional analytical computer modeling are used to define optimum duct configurations for any specific application.

The evaporation zone immediately follows the slurry injection zone and consists of a section of ductwork downstream of the atomizer that has no turns, transitions, or obstructions. Its length is established by the gas-to-slurry contact time necessary to attain surface dryness. While the exact residence time required for slurry injected by a rotary atomizer depends on gas temperatures, droplet sizes, and moisture-to-solids ratio, 0.5 seconds should yield dryness for droplets at typical duct temperatures (8).

The drift zone constitutes the remaining ductwork between the evaporation zone and the particulate collector. There are no special configuration requirements or restrictions at this stage of the process, since the entrained particles exhibit surface dryness. SO₂ absorption will continue to occur in the reaction product

interstices as long as free water is present. Therefore any additional gas-solids contact time should result in improved lime utilization.

Pilot Plant

The pilot plant was located at the Muskingum River Plant of Ohio Power and consists of three atomizer stations: (1) Station I installed in a 60 ft. (1 second residence time) vertical configuration, (2) Station II installed in a horizontal duct run with a 60 ft. (1 second residence time) evaporation zone, and (3) Station III also installed in horizontal ductwork, but with only a 30 ft. (1/2 second residence time) evaporation zone (9). The ductwork associated with the vertical configuration was cylindrical. All other ductwork in the plant had rectangular cross-section. Flue gas flowed sequentially through the three atomizer stations, to an ESP of weighted-wire design, through an induced-draft (ID) fan and back to the Unit 5 host ductwork.

Test Program

Pilot-plant testing began with the 250-mm (10-inch) rotary atomizer installed in the vertical duct section. The test protocol started with clear water at conservative conditions of maximum atomizer speed and peak gas flow, and proceeded through steps of increasing water feed rate. Duct wall thermocouples were used to determine the downstream droplet plume characteristics. Clear-water testing also evaluated various atomizer speeds and gas flow rates.

Testing continued with slurry injection in the vertical duct configuration. In addition to plume characterization, overall SO₂ removal was measured across a matrix of gas flow, temperature, and lime slurry levels. Product was collected and analyzed for chemical content. Performance data for the pilot precipitator was collected with and without the In-Duct Scrubbing process in operation. Gas-sampling and processing equipment automatically measured and recorded gas flow, SO₂, NO_x, O₂, CO₂, and moisture levels, as well as pressure drop for the gas treatment components in operation.

Tests were then performed in the horizontal ductwork (Station II). These began with a more detailed investigation of gas flow and temperature distribution than was undertaken in the vertical (Station I) testing. The clear-water phase and slurry testing routines were essentially similar to that performed for the vertical-duct configuration. The option to test at Station III was not exercised under this program.

Tests at gas conditions for enhanced NO_x removal, were investigated in the horizontal-ductwork arrangement. Dry sorbent was injected upstream of the atomizer to allow mixing prior to humidification. Tests were performed both with clear-water and slurry feed to the atomizer and for approach to saturation temperatures in the 40° to 60°F range. The resulting SO₂ and NO_x captures were determined and chemical analysis of reagent and product were obtained during tests involving slurry injection.

Results

Testing has been completed. The bulk of the data being presented was gathered at Station II, however the results from Station I are similar so that the information and conclusions can be presented on an integrated basis.

Gas Velocity Distribution --

Simultaneous measurements of gas velocity were obtained at 9 points of duct cross section immediately adjacent to the rotary atomizer and approximately 30 feet downstream. The sensing technique was a modified hot wire approach developed by Kurz Instruments Company. Data was obtained at a nominal flue gas flow of 50,000 cfm at 330°F for 3 locations in the 50 inch wide by 40 inch high duct without slurry or water addition. The discrete velocity measurements were analyzed by Golden Software's "SURFER" program and those profiles are presented in Figure 6. Immediately upstream (6 ft or 0.1 seconds residence time) of the atomizer the average gas velocity was 3656 feet per minute ($\pm$ a standard deviation (S.D.) of 369 fpm) indicating good closure with the 50,000 cfm volumetric flow established. The average velocity of the right side exceeded the left by about 8% and exceeded the average center velocity by 11%. Immediately downstream of the atomizer the average velocity was 3542 feet per minute ($\pm$ 485 fpm S.D.) the right side exceeded the left by 10% and the center by 15%. Furthermore the velocity at the bottom of the duct was greater than the velocity of the top of the duct. The presence of the atomizer created only minor variations in the flow profile.

At the 30 ft (0.5 second residence time) position the average velocity was 3377 feet per minute ($\pm$ 350 fpm S.D.). The right to left and right to center bias was more pronounced at 13% and 18% respectively. The lower standard deviation reflected less top to bottom variation in the gas flow.

Even though measurable gas velocity variations were observed, the standard deviations of less than $\pm$ 15% are typical for well designed duct work. Attempts to use the multi-point velocity probes during atomizer operation proved unsuccessful due to fouling and wetting of the sensing elements.

Gas Temperature Distribution --

Although velocity measurements during slurry injection could not be made temperature results were obtained and are presented in Figure 7. In the atomizer near field (6 ft or a 0.1 second residence time) significant temperature variation was observed with the left side about 10 degrees hotter than the right side and with a pronounced hot spot in the center of the duct. Further downstream, at the 30 ft point (a 0.5 second residence time), the duct temperature profile had smoothed considerably showing that good mixing had occurred. At this point the average gas temperature of 198°F indicates nearly complete evaporation since the slurry injection rate of 13.3 gpm should yield an equilibrium gas temperature of 190°F.

Duct Wall Temperature --

A grid of duct wall thermocouples proved to be effective in obtaining important process information. Differences between water injection and slurry injection at flow rates giving equivalent approaches to the adiabatic saturation temperature were observed. The considerably higher wall temperatures observed for the slurry case are attributed to the effects of lime solids which reduce surface tension resulting in smaller droplet sizes. Also, the lower fraction of water per individual droplet promotes more rapid evaporation.

The data clearly show that temperatures in the slurry case are within a few degrees of equilibrium after 8 ft (0.15 second residence time) whereas the water

injection data does not attain a similar level until 24 ft (0.4 second residence time).

Duct wall temperatures were also used to evaluate the efficacy of the use of several gas/droplet flow directing flaps. These devices were utilized to optimize the vertical and lateral components of gas velocity immediately upstream of the droplet atomization point. A significant increase in average floor temperature and a major downstream shift of the minimum floor temperature resulted from utilizing a vertical flap. Application of a lateral flow control device increased the average right wall temperature and eliminated a cold spot in the atomizer near field (130°F at 4 ft).

Atomizer Speed -- The inverse relationship of atomizer speed to droplet size was developed by Snaddon & Johnson (10). Data taken at three different atomizer speeds clearly show that higher wall temperatures, which are indicative of smaller droplet sizes, occur at faster atomizer rotation. In fact, at 14,100 rpm, the effect is especially significant within the first 18 ft (0.3 second residence time) after atomization. Rotational speeds in excess of 14,100 rpm were not possible with the atomizer used at the pilot facility.

In view of the favorable evidence for smaller droplets, atomizer speeds of 14,000 rpm and slurry solids contents approaching 25% were selected for parametric sulfur removal testing.

Sulfur Removal -- Parametric investigation of flue gas SO₂ reduction was conducted at both Station I and Station II. Data was taken for calcium to sulfur inlet molar ratios ranging from 0.4 to 1.5, and duct gas velocities from 28.8 to 69.6 feet per second. The observed SO₂ removal efficiencies fell into two distinct groups based on process temperature and are presented in Figure 8. Group 1 data comprised temperatures from 170°F to 185°F (40°F to 55°F approach to saturation). The correlation coefficient of 0.959 attests to the virtual linearity of the relationship between SO₂ removal and Ca to S inlet feed rate. The Group 2 data, taken at temperatures ranging from 185°F to 250°F (greater than 55°F approach to saturation), also fit a linear model however the steeper slope indicates a less efficient process condition. Demonstration of the ability to achieve the goal of 50% SO₂ removal at a Ca to S molar ratio of 1.47 was verified experimentally by Group 1 data. The projected Group 2 Ca to S molar ratio objective of 1.61 could not be verified experimentally due to a maximum of 25% lime slurry solids that can be attained in detention type slakers. Both groups of data clearly demonstrate the stability and reproducibility of the IDS process.

Based on chemical analysis of material collected in the ESP during a typical run, fly ash components (SiO₂, Fe₂O₃, Al₂O₃ and inerts) comprise 53% of the collected material. Reagent conversion, based on moles of calcium available, is 11% to carbonate and 36% to sulfur compounds. This is in good agreement with the projected lime utilization of 35% calculated for a Ca/S molar ratio of 1.1 at an SO₂ removal efficiency of 39%.

Precipitator Performance --

ESP performance data taken during testing at Station I are presented in Table 3. At a Specific Collecting Area (SCA) of 360 ft²/1000 acfm, outlet opacities showed a linear relationship to total inlet loading (fly ash and lime products) exhibiting a 0.916 correlation coefficient. Further, opacity, when normalized to

a constant inlet grain loading, showed the expected inverse relationship to specific collection area energized ($r = 0.778$).

Station II precipitator studies first focused on voltage-to-current (V-I) relationships. Data were collected for both a fly ash only case (about 3.9 gr/acf) and a slurry injection case (about 8.1 gr/acf). No notable differences in the V-I curves are apparent for the outlet and center fields with only the inlet field showing a significant increase in secondary voltage resulting from the higher particulate loading. As increasingly higher loadings are encountered, it is anticipated that the center fields V-I relationship would be impacted.

Precipitator parametric data for a typical slurry injection test confirm that more than 92% of the material is collected in the inlet hopper. V-I data indicate the preponderant effect is absorbed by the inlet field with reduced current in the second field probably resulting from loading effects. The electrostatic precipitator data obtained indicate stable and predictable performance.

Dry Recycle --

Experimental efforts at the IDS pilot facility concluded with an evaluation of reinjection of dry off-product (spent lime sorbent) upstream of the slurry atomization zone. Tests were conducted at various gas flows, temperatures, recycle rates, and lime slurry flows. The results plotted in Figure 9 show that SO_2 removal is strongly related to the amount of calcium injected as a slurry ($r = 0.959$) with little apparent influence due to recycle rate or available lime. As compared to single pass slurry treatment (see Figure 8), the required Ca to S molar ratio for 50% SO_2 removal is reduced from 1.5 to 1.0 by the very presence of off-product material at a nominal recycle rate of 4.0 gr/acf. A similar enhancement effect for the use of wet recycle in dry flue gas desulfurization testing has been reported (11).

Measurements of flue gas NO_x concentrations also comprised part of the dry recycle testing. NO_x reductions of 11 to 18% were observed. No apparent relationship is noted with regard to SO_2 removal, lime feed rate or recycle lime content, leaving unanswered the question of whether the IDS process can be optimized for NO_x removals approaching the 50% goal desired for acid rain precursors.

Precipitator outlet opacity data were also acquired during dry recycle testing. Although correlations were only in the moderate range ($r = 0.613$), there appears to be a linear relationship between the dry recycle flue gas concentration and opacity. The data confirm the ability of the precipitator to accept significantly higher inlet loadings with only minor reduction in performance. This result is consistent with the V-I data observed during parametric testing.

HUMIDIFICATION SCALE-UP USING MULTIPLE NOZZLE ARRAYS

Humidification field tests with arrays of nozzles conducted at the HALT pilot unit at Ohio Edison's Toronto Station demonstrated a method of humidifier scale-up from single-nozzle pilot test data. The scale-up method uses arrays of nozzles, with each individual nozzle operated at fixed conditions determined as optimum in single-nozzle tests. By applying this method, the Consolidation Coal Company (Consol) 8.3-inch diameter pilot humidifier operation with a single Spraying Systems 1/8JJ-J12 (J12) nozzle was successfully scaled up to operation of the 31-inch square Toronto Station humidifier with arrays of up to 46 J12 nozzles.

Approaches to the adiabatic saturation temperature as low as 20°F were achieved without wall wetting or wet solids deposition problems. A uniform flue gas distribution was very important for good humidifier operability. Spray plume overlap did not significantly impair humidifier operability. The tests provided data on nozzle deposition and solids dropout that may be useful for large-scale humidifier design.

Test Program

The objective of the nozzle array field test program was to evaluate a humidifier scale-up method (see Figure 10). In this method, an array of two-fluid nozzles is used to humidify the flue gas. Each nozzle in the array is operated at fixed conditions (water and atomizing air flows and pressures) determined to be optimum in single-nozzle pilot tests with a cylindrical humidifier. The number of nozzles determines the total water flow and the approach to the adiabatic saturation temperature. The nozzles in the array are spaced so that humidification performance is not impaired by nozzle-nozzle interactions. The radius of the pilot humidifier defines the minimum nozzle-wall distance in the nozzle array. It is assumed that each nozzle will successfully humidify the same cylindrical volume of flue gas as the single nozzle in pilot tests (see Figure 11).

The field tests were conducted to evaluate this method for scale-up from the Consol 8.3-inch internal diameter cylindrical downflow pilot humidifier to the 31-inch square horizontal humidifier at Ohio Edison's Toronto Station. In the 8.3-inch diameter pilot unit, a single Spraying Systems J12 nozzle was used to humidify 175 scfm of 300°F flue gas (superficial gas velocity of approximately 11 ft/sec) to 20°F to 30°F approaches to saturation with no serious wall wetting or wet solids deposition problems. Optimum nozzle operating conditions were identified for good humidifier operability. In the field tests, five different J12 nozzle arrays were tested containing 9, 13, 16, 25 and 46 nozzles. Each nozzle was operated at conditions determined in the pilot unit (see Table 4). The minimum nozzle-wall spacing was five inches, slightly larger than in pilot testing where the minimum nozzle-wall spacing was 4.15 inches.

The base tests made with arrays of 9, 13, and 16 nozzles were conducted at an inlet flue gas superficial velocity of 14 ft/sec and an inlet temperature of 280°F in order to maintain similarity with pilot unit operation and demonstrate the scale-up method. The humidification water requirement per unit cross section of flue gas was the same as in the pilot tests and there was minimal overlap of nozzle spray plumes (assuming 8.3-inch diameter spray plumes and minimal cross mixing in the duct). With a fixed water throughput of 4 gph per nozzle, the 9, 13, and 16 nozzle arrays allowed humidification to 70°F, 45°F and 25°F approaches to the adiabatic saturation temperature, respectively.

The tests with arrays of 25 and 46 nozzles (see Figure 12) allowed humidification to a 20°F approach to the adiabatic saturation temperature at inlet flue gas velocities of 23 ft/sec and 35 ft/sec, respectively. The water throughput per nozzle remained fixed at 4 gph, so increasing the number of nozzles allowed more flue gas to be humidified. In these tests, there was significant overlap of the spray plumes and the water flow per unit flue gas area was greater than in the pilot tests. Inlet flue gas temperatures were 280°F and 300°F to 315°F in the 25- and 46-nozzle tests, respectively.

Results and Discussion

The field tests demonstrated the humidifier scale-up method from single-nozzle pilot test data using arrays of nozzles. In the tests, the Consol 8.3-inch cylindrical, vertical pilot humidifier operation was scaled-up to a 31-inch square, horizontal humidifier. In the tests with the 9, 13, and 16 nozzle arrays, the desired approaches to adiabatic saturation of 70°F, 45°F, and 25°F were achieved, respectively, with no serious operating problems such as wall wetting or wet solids deposition. These tests had the same 14 ft/sec inlet flue gas velocity. In the tests with the 25- and 46-nozzle arrays, approaches to adiabatic saturation down to 20°F were achieved with no operating problems. The inlet flue gas velocities were 23 and 35 ft/sec in the 25- and 46-nozzle tests, respectively. The 16-, 25- and 46-nozzle tests operated at 20°F to 25°F approach. Measured droplet drying times were 0.8 seconds to 1.2 seconds (see Table 5) and were similar to those observed in the pilot tests at a 25°F approach. In the 9- and 13-nozzle tests operated at 70°F and 45°F approaches, respectively, the drying time was shorter and consistent with that observed in corresponding pilot tests. Humidifier operability was generally better in the high flue gas velocity tests (23 and 35 ft/sec) than in the base tests made at a velocity of 14 ft/sec. Each multiple nozzle array test consisted of 6 to 17 hours of humidifier operation.

The successful results from the 9-, 13- and 16-nozzle tests, which had minimal overlap of spray plumes (see Figure 11), indicate that the scaled-up humidifier may be designed by considering it as a collection of non-interacting parallel humidification zones, with the performance of each zone resembling that of the single-nozzle pilot humidifier as shown in Figure 10. The successful results from the 25- and 46-nozzle tests expanded the flexibility of the humidifier scale-up method by showing that significant overlap of the spray plumes or the humidification zones is acceptable. In these tests, approaches of 20°F and below were achieved with inlet flue gas velocities of 23 ft/sec and 35 ft/sec. Data presented in Table 5 shows that the measured drying time increased slightly to about 1.2 seconds in the 46-nozzle test; however, this may have been due partly to the lower nozzle atomizing air pressure used in this test and to the lower approach temperature.

The absence of wall wetting was confirmed by measuring duct wall temperatures during each of the tests. For example, skin temperature profiles along the four duct walls as a function of distance from the nozzle array for the 25-nozzle test at a 22°F approach are provided in Figure 13. The minimum duct wall temperatures observed were at least 10°F above the adiabatic saturation (wet bulb) temperature, indicating dryness. Past experience has shown that the wall temperature drops to the wet bulb temperature when the wall is wetted (12). The dryness of the walls was further confirmed by visual observation during testing and by the absence of wet or hard deposits after testing, as discussed below.

After each of the field tests, the humidifier internals were inspected. No wet or hard solids deposits were observed. Some ash and hydrated lime adhered to the duct walls; however, these deposits were always dry and loose and fell off after reaching a certain thickness (1/16 to 1/4 inch). The amount of material which adhered to the walls was less in the tests with higher flue gas velocity. There was substantial drop-out of dry solids on the duct floor in the 9-, 13- and 16-nozzle tests made at the low flue gas velocity (14 ft/sec inlet). In all cases, this material was soft and loose and was removed easily by raising the flue gas velocity momentarily. Some drop-out occurred in tests at flue gas velocities up

to 35 ft/sec; however, it was much less than in the low velocity tests. The results indicate that some means of removing solids dropout may be required if the humidifier design velocity is low. Another important observation from the field tests was that a uniform flue gas flow distribution was critical for good humidifier operability.

An initial 16-nozzle array test was not successful because of a significantly skewed flue gas velocity profile. The flue gas velocity was higher (16 to 17 ft/sec) near one side wall of the duct than near the opposite side wall (12 to 13 ft/sec). In this test, wall wetting and wet solids deposition were observed even at a 50°F approach to the adiabatic saturation temperature. Duct wall temperatures were at the wet bulb on the low velocity side of the duct and on the duct floor 2 to 4 feet downstream of the nozzle array. Visual observation indicated that there was a film of water on the duct wall, a puddle of water on the duct floor, and the formation of a wet solids deposit. Straightening the flue gas flow by means of a perforated plate upstream of the nozzle array eliminated these problems and allowed the successful tests as discussed earlier.

In the field tests, deposits on the nozzle array were significantly larger than those observed on the single nozzle in the pilot tests. The solids deposition on the nozzles did not adversely affect nozzle atomization performance during the 6 to 17 hour test periods, based on steady humidifier performance observed during the tests. However, the observed deposition indicates that a means of preventing or removing solids deposits on the nozzles may be needed for long-term humidifier operation.

FUTURE RESEARCH FOR THE DEVELOPMENT OF DUCT INJECTION TECHNOLOGY

ANALYSIS OF RESEARCH GOALS

The development of duct injection technology is being pursued to provide cost-effective control of SO₂ emissions that addresses the unique problems of existing, uncontrolled, coal-fired utility boilers. These pre-NSPS boilers have (1) a limited remaining service life, (2) low-capacity factors, (3) limited available space, (4) difficult access, and (5) a requirement to buy replacement power during the time required to install emissions control technology.

Currently available technology (lime and limestone scrubbers) requires a significant capital investment and a suitably large area to place the equipment; it is not compatible with the unique problems associated with the majority of units in the pre-NSPS boiler population. Duct injection technology, however, is projected to (1) have low capital cost, (2) have moderate operating cost, (3) use existing equipment and therefore require minimal changes to the existing system, and (4) be simple to install and operate. The use of existing ductwork for the reaction vessel substantially reduces capital and space requirements.

The criteria established for the development of duct injection technology were to (1) achieve greater than 50% SO₂ removal, (2) obtain greater than 35% sorbent utilization, (3) produce an acceptable dry waste material, and (4) reduce the cost of emissions control technology to less than \$500 per ton of SO₂ removed. The proof-of-concept tests conducted by Dravo Corporation, Bechtel National, Inc., and General Electric Environmental Systems met the minimum goals of the U.S. Department of Energy's Duct Injection Technology Development program. However, these tests also demonstrated that a better scientific understanding of the

process and a more comprehensive engineering design basis are needed to achieve commercial readiness. Areas of concern include the following:

- o Sorbent reactivity and behavior
- o Transport and chemical processes within the duct
- o Hydrodynamics of the system
- o Nozzle design and operation
- o Humidification system design
- o Wall deposition of sorbent materials and fly ash
- o ESP performance
- o Disposal of the dry waste material

It was determined that additional efforts are required to address these areas of concern and to develop the engineering design criteria applicable to a range of boiler sizes, flue gas concentrations, and duct configurations necessary for the installation of this technology on a significant fraction of the population of existing coal-fired utility boilers. A comprehensive research program was established in 1988 to complete the technology base required to (1) ensure adequate performance at operating scales, (2) verify the design basis, and (3) establish the reliability of duct injection technology. This comprehensive research program includes the following:

- o A survey of 484 coal-fired utility boilers to determine existing duct configurations
- o Fundamental research to gain an understanding of the physical and chemical phenomena occurring in the system
- o Development of engineering design criteria and a scaleup methodology
- o Publication of a design handbook and predictive computerized process model

DUCT CONFIGURATION SURVEY RESULTS

The duct configuration survey was conducted to provide a general design basis for existing duct configurations at selected plants. This will allow the Office of Fossil Energy to further refine the Duct Injection Technology effort. The survey's results are critical to the success of the overall duct injection program because they will be used to determine the ranges of various parameters and operating conditions required for the full-scale application of duct-injection technology. Analysis of the survey results also allows the prediction of optimum operating conditions and component designs needed to move the technology towards commercialization in a timely manner.

Survey requests were restricted to operating coal-fired utility boilers without FGD scrubbers that were built before or grandfathered under the Clean Air Act and whose 1986 emissions of SO_2 were calculated to be 1.8 lbs of SO_2 /MMBtu or higher. Further restrictions were that these units should be currently in operation at sites with an aggregate, coal-fired generating capacity of greater than 50 megawatts and should be no more than 35 years old.

The survey also provided a mechanism for direct industry input at an early stage of the research effort. This involvement is critical to the success of the program. The results of the survey were assembled into a data base to support the development of engineering design criteria and a predictive computer model that will be used in the design and construction of operating-scale duct injection units. This data base is now part of DOE's National Energy Technology Data Base, which is maintained at the Pittsburgh Energy Technology Center.

Survey Details

Utility Data Institute of Washington, D.C., a non-profit data compilation firm associated with the Edison Electric Institute, was retained by Burns and Roe Services Corporation, the on-site technical support contractor at DOE's Pittsburgh Energy Technology Center (PETC), to distribute the "Boiler Duct Description Report" survey form (Office of Management and Budget Control No. 1910-1400) to utilities meeting the requirements of the survey.

The first mailing of the survey form packages was made in early December 1987. A second follow-up mailing was made in early February 1988 with a requested response deadline of April 1, 1988. Additionally, individual utilities were contacted to further explain the purpose and importance of the survey and to request the utility's cooperation.

Any questionable information supplied as responses was reviewed and verified by directly calling the person identified on the form as the company contact. Required changes were made so that all responses could be correctly entered into the Boiler Duct Survey Data Base. The Boiler Duct Survey Data Base was designed to be an accessible data base that could be easily updated as needed.

Duct Survey Responses

Using PETC's coal-fired boiler utility data base, 484 candidate boilers were identified. These 484 boilers emit just over 8 million tons of SO₂ per year (see Table 6). It should be noted that this survey was voluntary (utilities were not required to reply); yet, the response rate as shown in Table 11 was nearly 70%. This is an excellent response for a voluntary survey of this nature. With few exceptions, the utilities were extremely cooperative.

Of the 340 boiler units for which information was received, 16 are equipped with hot-side ESP's. Since these 16 units represent less than 5% of the survey response, the results presented in this discussion will focus on the 324 units that are equipped with either cold-side ESP's or baghouses.

Tables 6 through 11 and Figure 14 summarize survey results for responses received on the returned "Boiler Duct Description Report" forms. The responses were categorized by the number of units and total capacity in megawatts (MWe) for each response category. Interestingly, the calculated percentages for either number of units or total capacity (MWe) determined for each category were approximately the same.

A brief summary of the results is described below:

- o The shape of utility boiler ducts is overwhelmingly rectangular (86.6% of the units surveyed representing 70,027 MWe).

- o Most of the utility boilers have either one or two ducts, with two ducts being the norm.
- o The majority of utility boilers have a cross-sectional area less than 300 square feet (ft²), with the range of 100 ft² to 300 ft² being the norm (see Table 7).
- o Approximately 40 percent (%) of the boilers have a total duct work length of 100 feet (ft) or more (see Table 8).
- o The flue gas temperature in the duct is usually below 350°F with the average calculated temperature being 316°F.
- o At 100% boiler load, the average flue gas velocity is 47 ft/sec. About 36% of the units have a velocity between 50 ft/sec and 70 ft/sec. At 75% load, the average calculated velocity drops to 35 ft/sec (see Table 9).
- o The longest straight duct run average value is 54 ft. The longest straight run is important because it determines drying time (see Table 10).
- o Two-thirds of the longest straight runs were reported to be horizontal (30° angle maximum) rather than vertical.
- o Two-thirds of the longest straight run cross-sectional dimensions were reported to be constant.

Another important parameter, the length of duct after the longest straight run leading to the entrance to the particulate collector, impacts both total residence time and overall SO₂ removal. A wide variation in the response is depicted in Table 11, with 66 units feeding directly from the longest straight run into the particulate collector, while 50 units were reported to have at least 50 feet of additional ductwork.

Survey questions about additional boiler fan capacity and the space available to accommodate more particulate equipment relied on the utility contact person's judgment and perception in filling out the survey form rather than on actual measurement. About half of the units were reported to need minimal modification in order to handle an additional 5 inches of water column (WC) fan capacity using the existing fan. Also, about half of the units were reported to be able to accommodate a 50% increase in the size of the particulate collector layout area.

Graphical results from a computer analysis of the data are shown in Figure 14. In this figure, the drying time available is considered at various boiler loads. Boiler load determines the flue gas velocity that was used to calculate drying time. The total residence time available includes the longest straight run and any additional downstream ductwork.

DESCRIPTION OF DOE'S COMPREHENSIVE RESEARCH PROGRAM

The goal of the Duct Injection Technology Development Program is to sufficiently expand the current knowledge base to bring the technology to a point of commercial readiness by 1992. This program, as presently conceived, consists of four

component parts: exploratory research and development, engineering development, system integration, and validation of the design basis. It involves the development of an engineering design base that will (1) support application of the technology to coal-fired utility boilers for the control of SO₂ emissions if required by possible future acid rain legislation, (2) allow confident predictions of system performance at operating scales, (3) be applicable to a range of boiler sizes, flue gas component concentrations, and duct configurations, and (4) provide a foundation for further (non-federal) development of the technology. To accomplish this goal, the efforts begun in 1985 to evaluate the technology have been expanded in a manner that provides for a comprehensive development program. The projected five-year program is a tightly integrated one, with a high degree of schedule overlap and interdependency prevailing between various portions of the program. Issues requiring resolution, and data requirements have been identified and included in a multiple project effort that will result in the publication of a design handbook in 1992. In addition, the design basis for duct injection technology developed under this program will be validated by tests conducted at a full-scale operating power plant (60 MWe to 100 MWe) through collaborative efforts with the Clean Coal Technology Program.

The comprehensive Duct Injection Development Program consists of the following elements:

- o Duct Configuration Survey
 - Burns and Roe Services Corporation
- o Enhanced Sorbent Utilization
 - Energy and Environmental Research Corporation
 - Acurex, Inc.
- o Fundamental Investigations of Duct and ESP Phenomena
 - Radian, Inc.
- o Scale-up Tests and Supporting Research
 - Gilbert Commonwealth, Inc.
- o Duct Injection Technology Prototype Development
 - United Engineers and Constructors, Inc.

A description of the teaming, scope, and duration associated with these efforts is provided in Tables 12 through 16.

The two projects being conducted under the Enhanced Sorbent Utilization element of the program are performing bench-scale experiments to determine controlling mass transfer resistances and to develop novel techniques to improve sorbent utilization.

Radian, and the team of organizations that they have established under the Fundamental Investigation of Duct and ESP Phenomena element of the program, will be conducting tests using a slipstream of flue gas (equivalent to 1 MWe) from the Meredosia plant of Central Illinois Public Service. These fundamental investigations will (1) determine the effect of droplet size and water evaporation rate on process performance, (2) conduct ESP performance evaluation and upgrading studies, (3) investigate the cleanability of wall deposits, (4) study the effect of lime particle size and slaking conditions on process performance, (5) evaluate sorbent

recycle, and (6) develop a first-generation computerized mathematical model of duct injection and ESP performance.

The contractor performing the effort entitled Scale-up Tests and Supporting Research, Gilbert Commonwealth aided by Southern Research Institute, will be using DOE's existing 12-MWe duct injection test unit located at the Muskingum River Station of Ohio Power in Beverly, Ohio. This project will (1) obtain engineering design data for both slurry and dry sorbent injection, (2) provide scale-up data for humidification and ESP performance, (3) develop and test process-control systems, and (4) validate process models developed under other parts of the program.

United Engineers and Constructors, in conjunction with Babcock and Wilcox, will conduct the Duct Injection Technology Prototype Development element of the program. This effort will be based on the information obtained by the other contractors in the program. United Engineers and Constructors will (1) develop engineering design criteria and a scale-up methodology, (2) complete the development of a second-generation predictive process model of duct injection and ESP performance that will serve as a design tool, (3) evaluate and characterize waste materials, (4) develop improved nozzles for atomization of water and slurries of slaked lime and water, and (5) prepare and publish a design handbook that will provide the information necessary for application of duct injection technology to pre-NSPS coal-fired utility boilers.

In addition to the design handbook that will serve as the final product of this effort, each of the teams involved in the program will publish reports on completed segments of work. Twenty-seven individual topical reports will result from this program. A list of these reports is provided in Table 17.

At the completion of the Duct Injection Technology Development program, utility companies evaluating the installation of SO₂ emissions control technologies at an existing plant will have sufficient information to determine whether duct injection technology is best suited for their specific needs. And when a utility decides to install a duct injection system, a sound engineering design basis will be available, allowing them to confidently complete the detailed engineering required.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

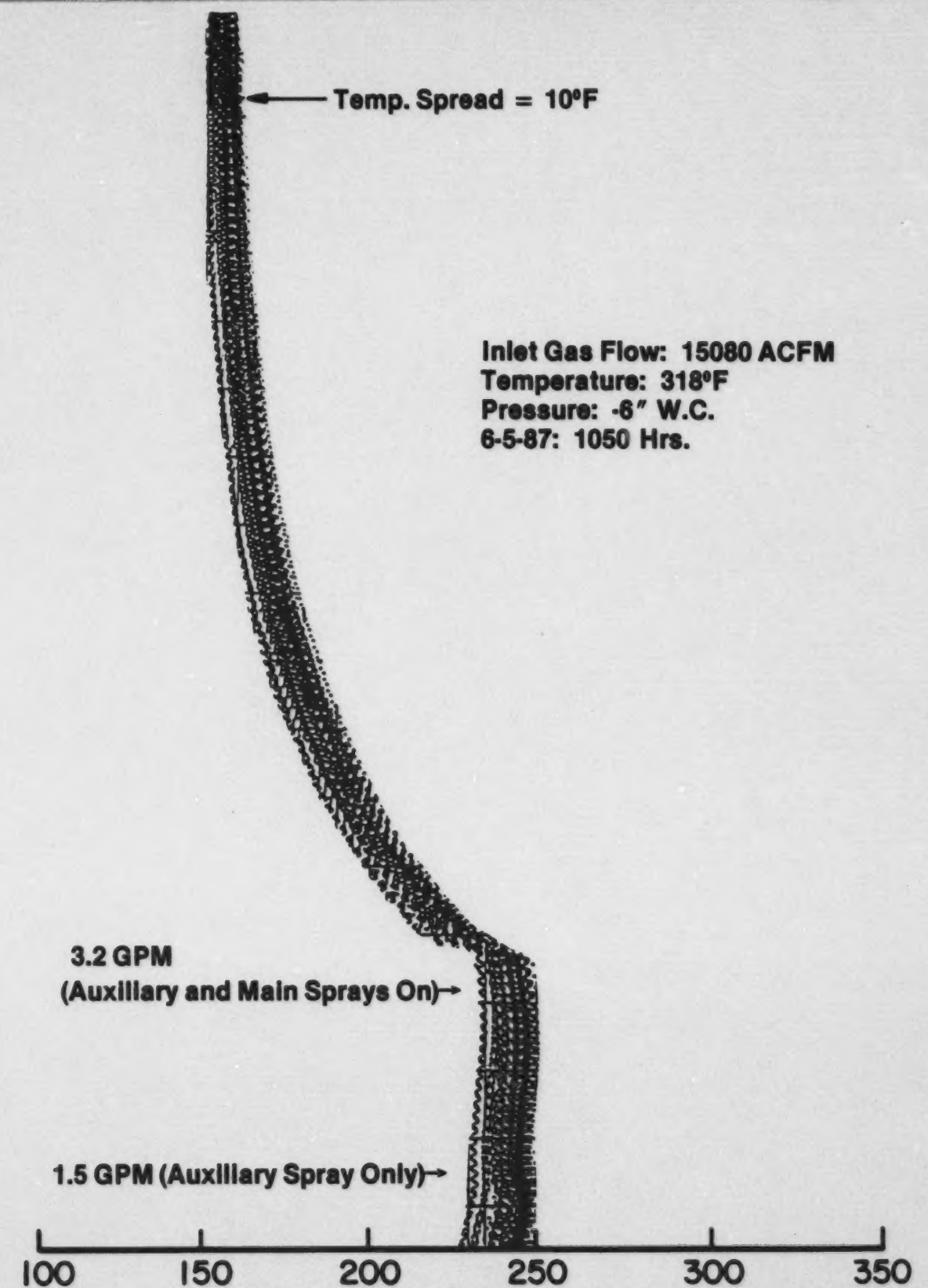


**Figure 1. Stripchart Recorder: Effect of Auxiliary Spray.
(Chart Speed 6"/Hour)**

**Figure 2. Hydrate Utilization
(Upstream Injection — Disk 23)**

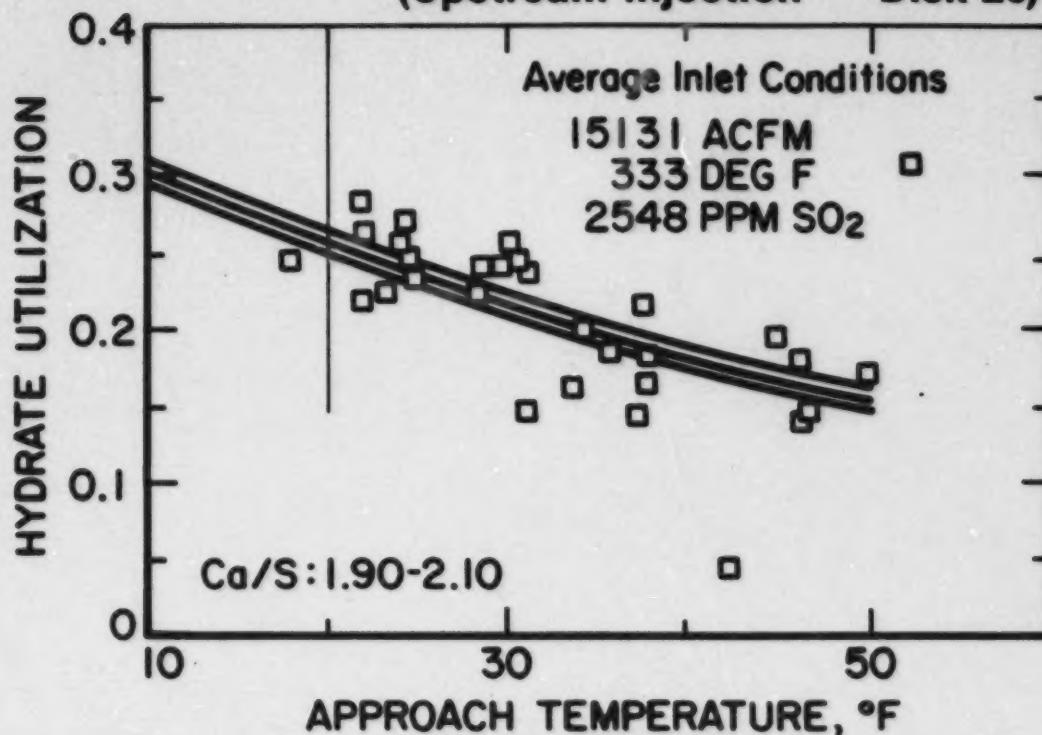
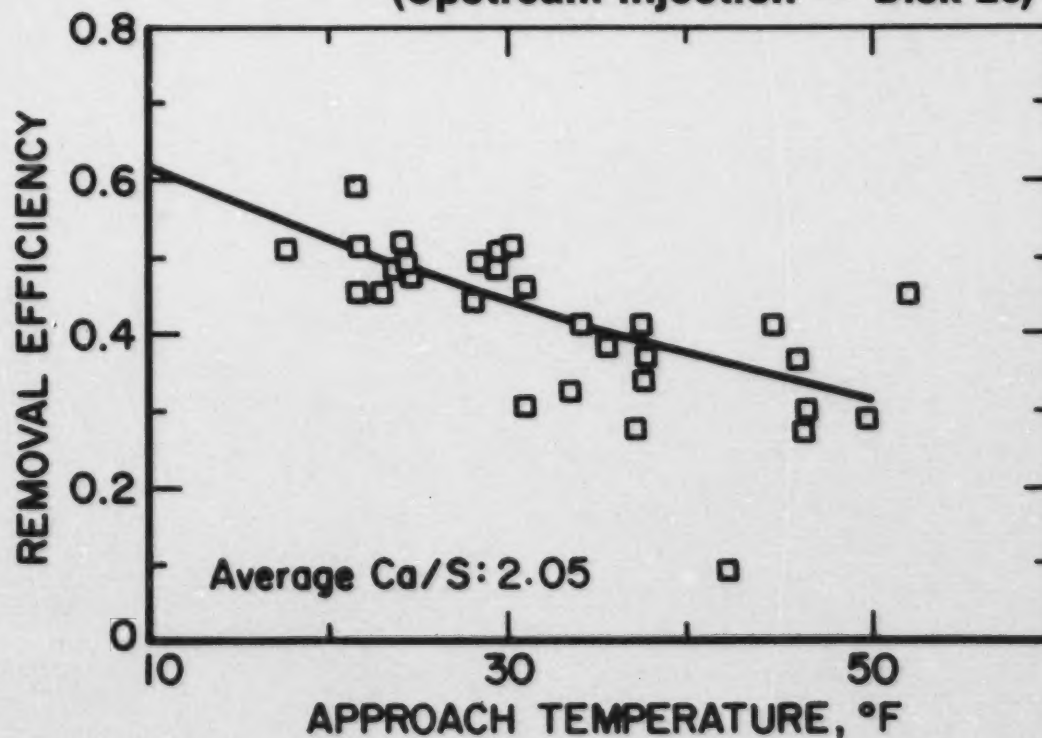


**Figure 3. Removal Efficiency
(Upstream Injection — Disk 23)**



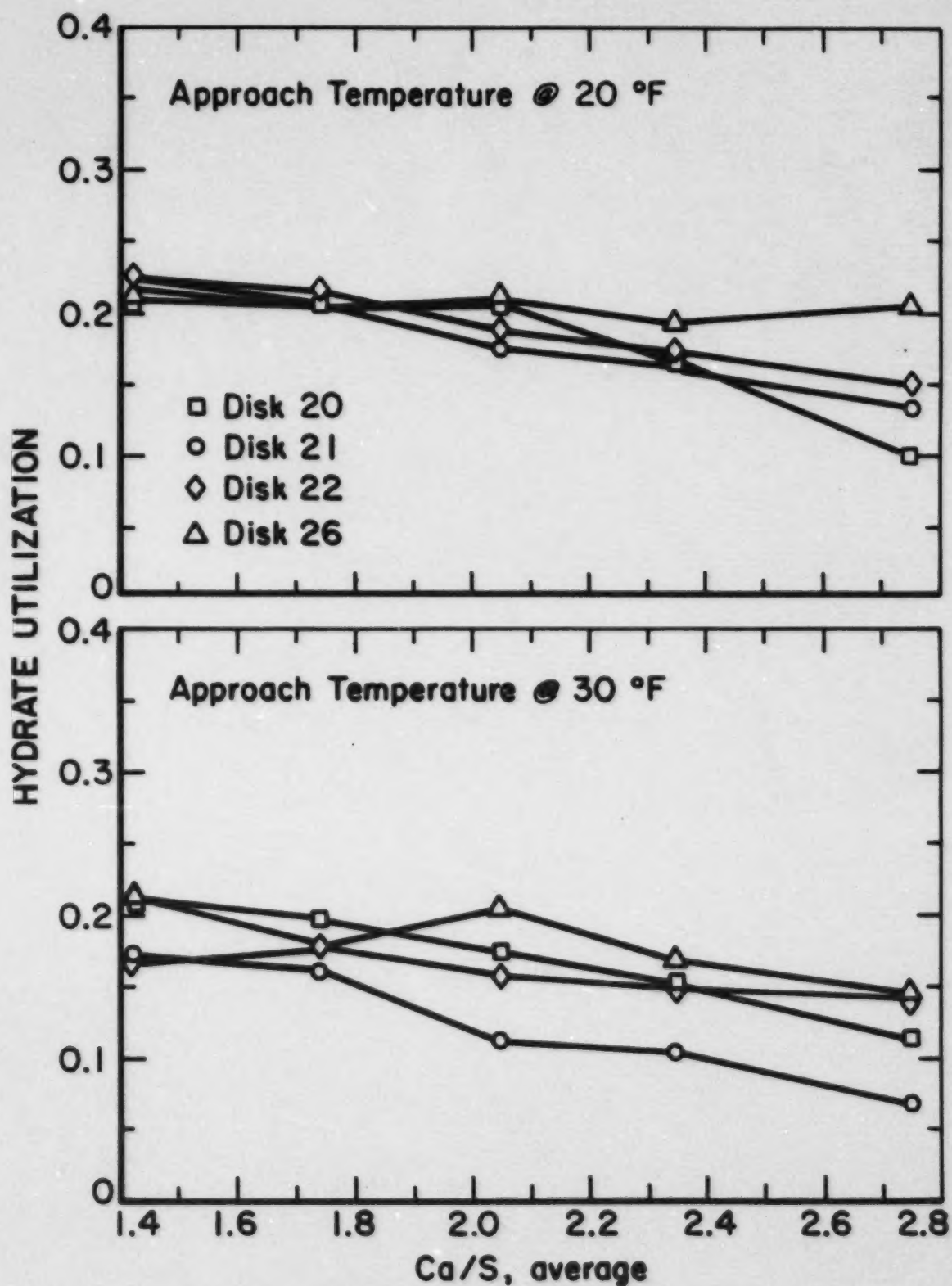


Figure 4. Effect of Approach Temperature.

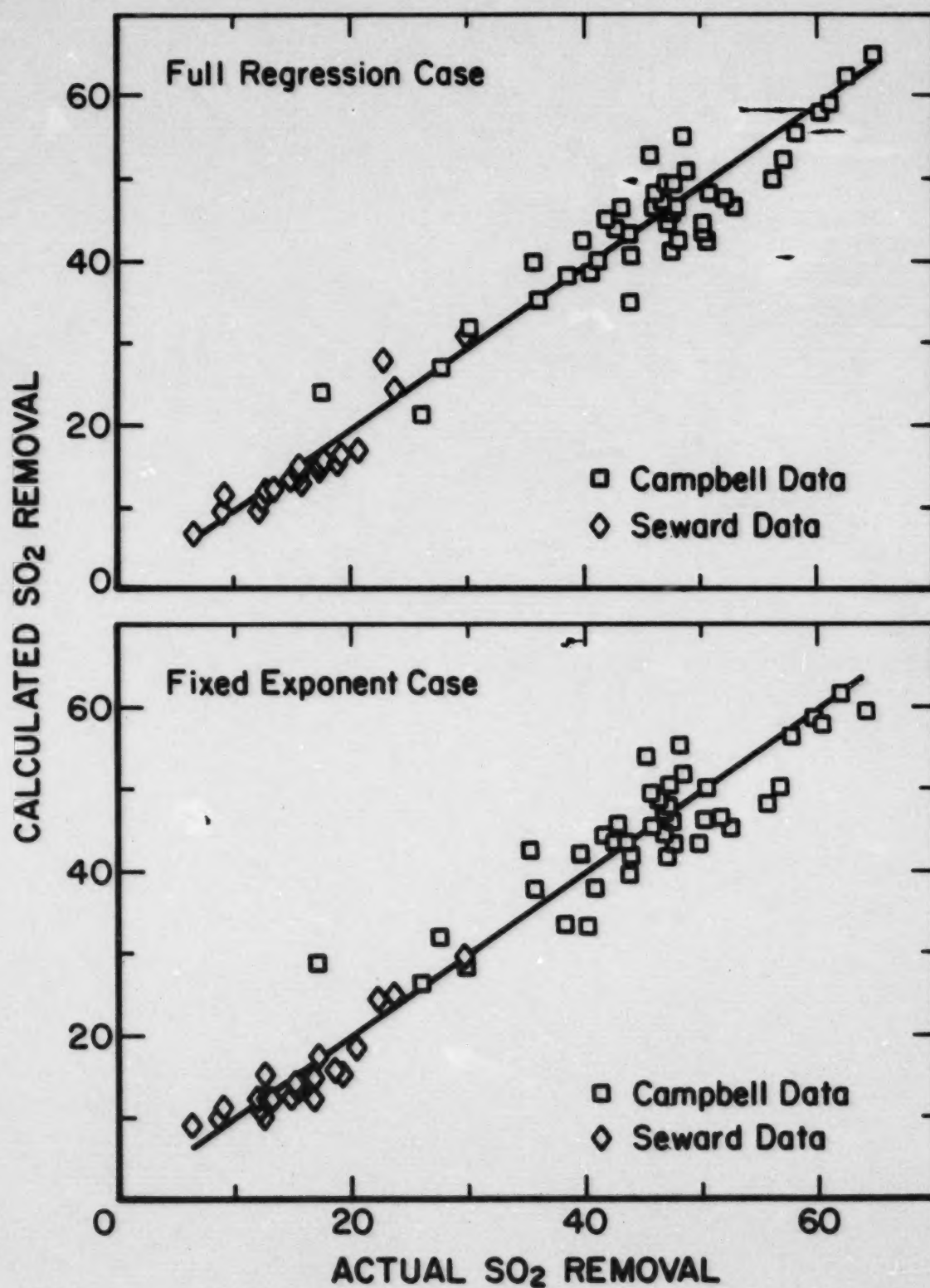


Figure 5. Calculated vs. Actual SO₂ Removal.

Figure 6. DOE-IDS Gas Velocity Data - Station II

50 Kacfm, 330°F

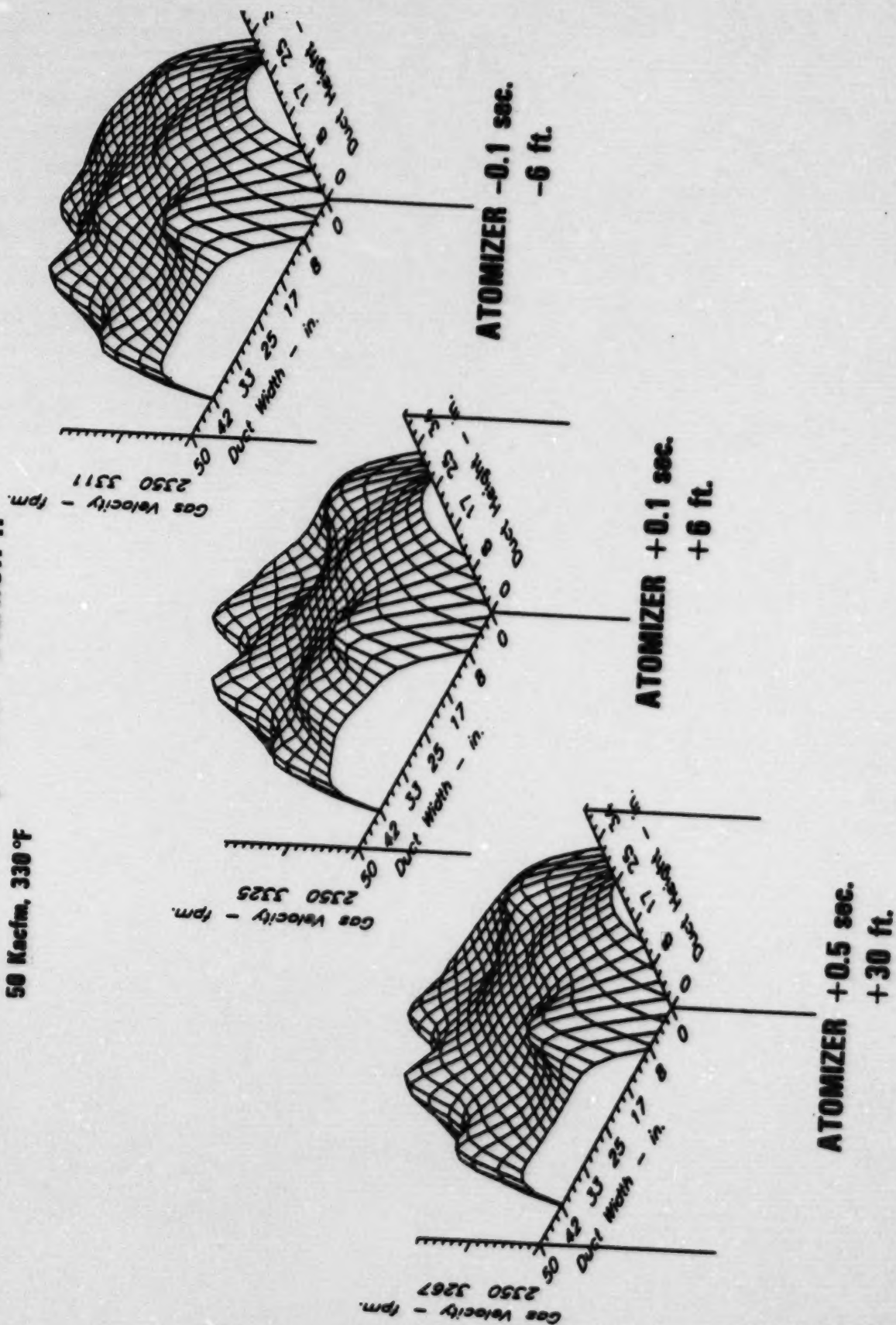
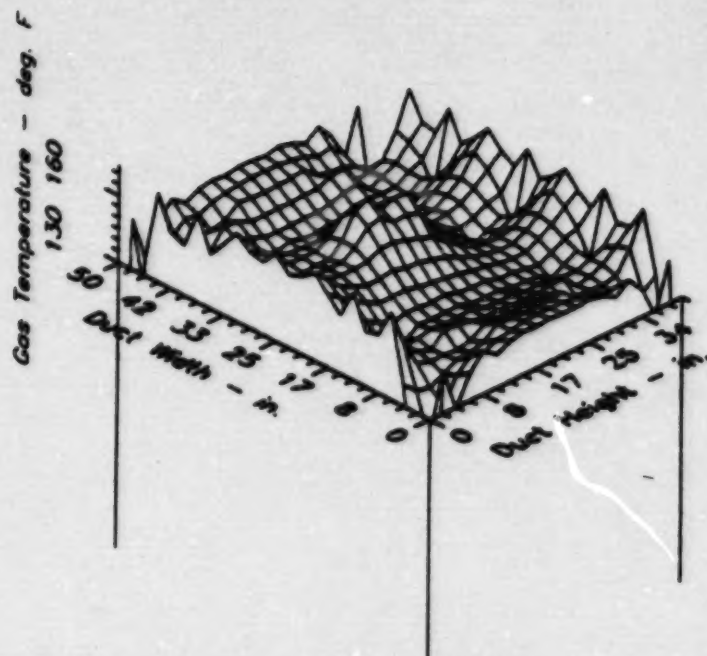
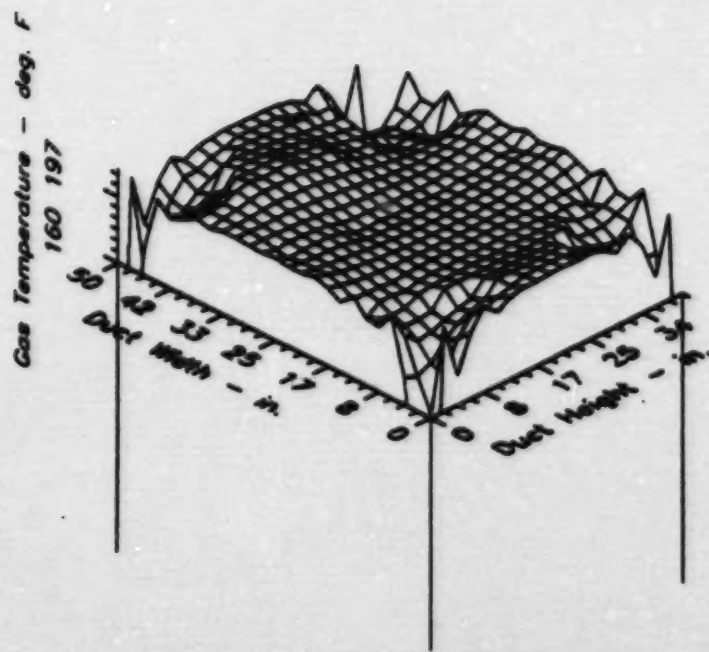


Figure 7. DOE-IDS Temperature Profile Data - Station II
50 Kacfm, 13.3 gpm slurry, 14 Krpm



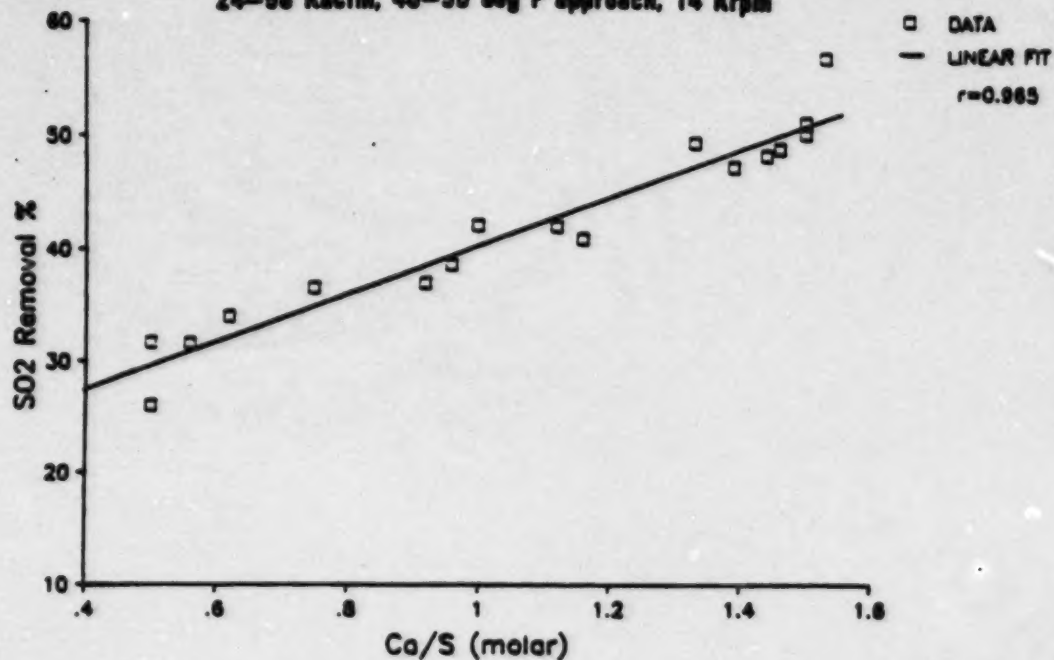
**GAS TEMPERATURE, ATOMIZER +0.1 sec.
+6 ft.**



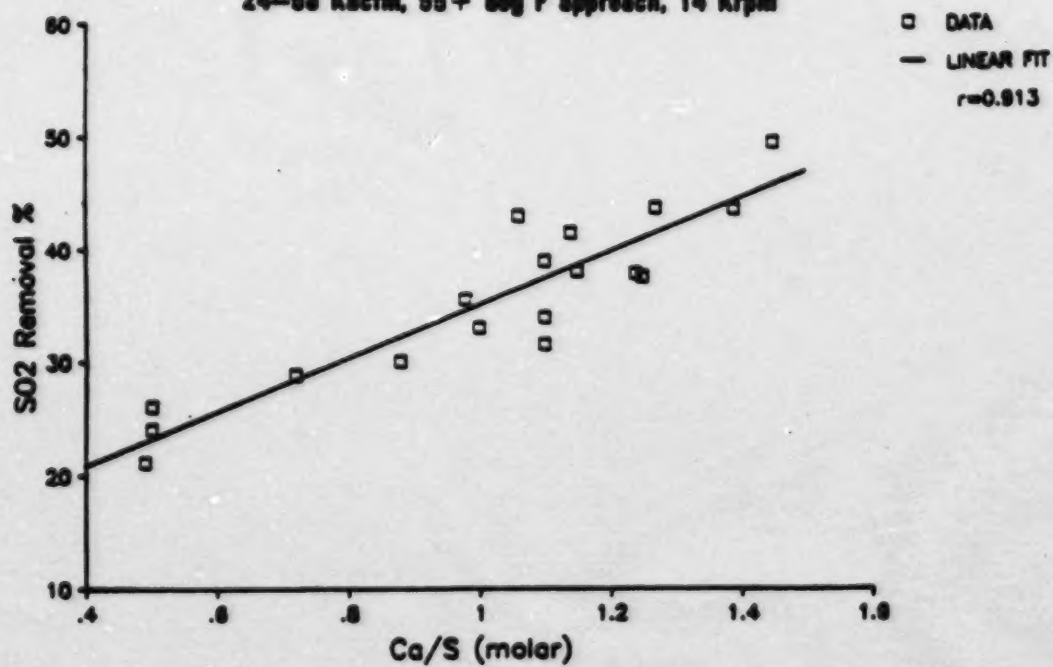
**GAS TEMPERATURE, ATOMIZER +0.5 sec.
+30 ft.**

Figure 8. DOE-IDS Slurry Data - Stations I & II

24-58 Kacfm, 40-55 deg F approach, 14 Krpm



24-58 Kacfm, 55+ deg F approach, 14 Krpm



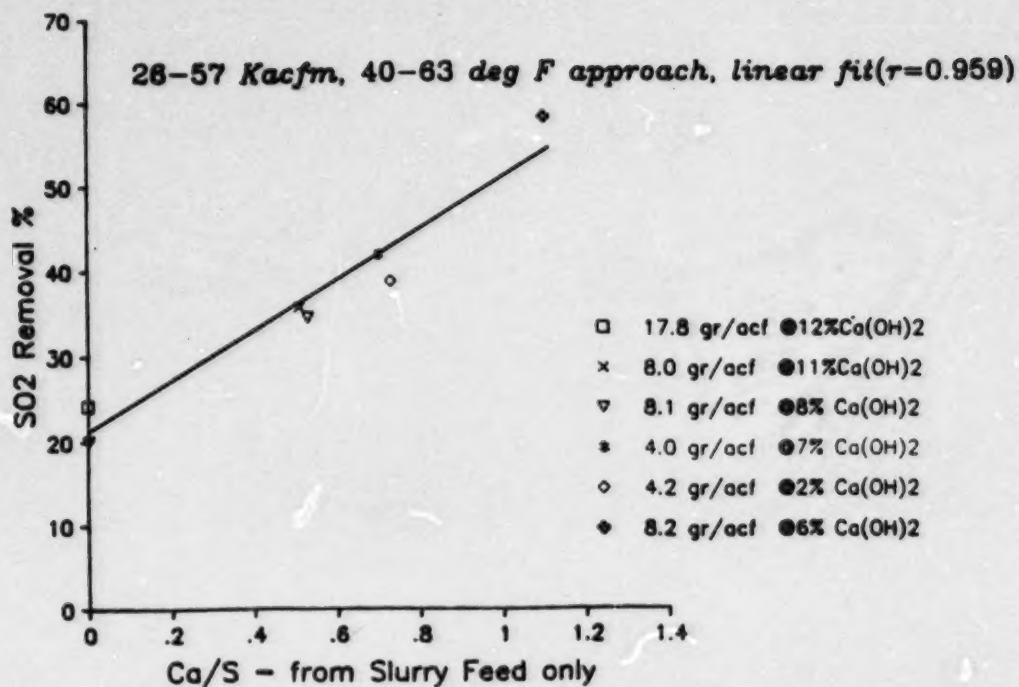


Figure 9. DOE-IDS Recycle Data - Station II

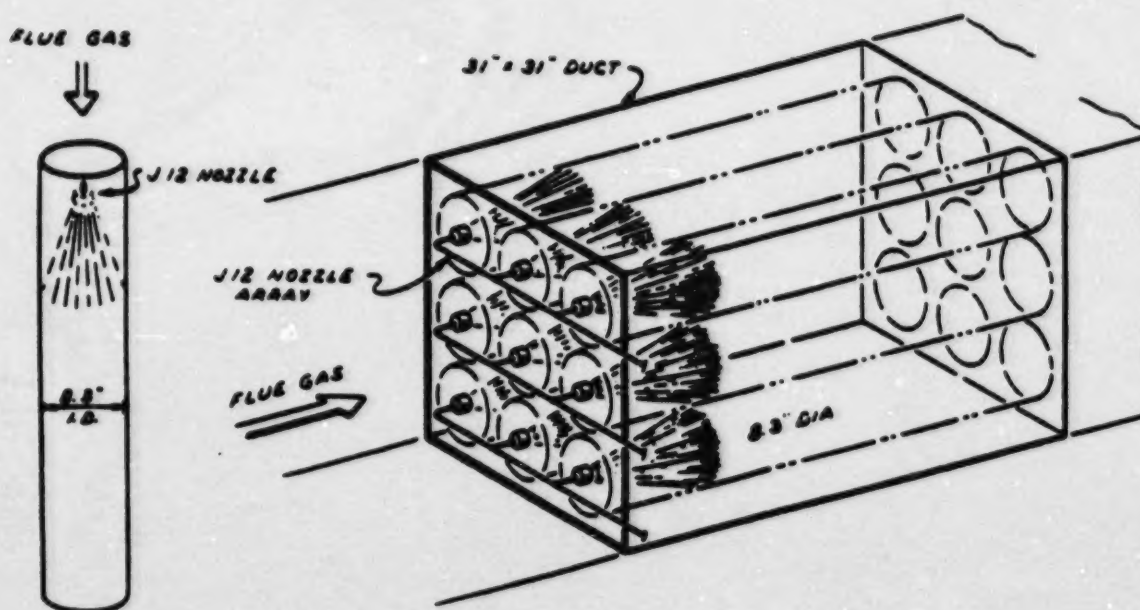


Figure 10. Humidifier Scale-Up Method

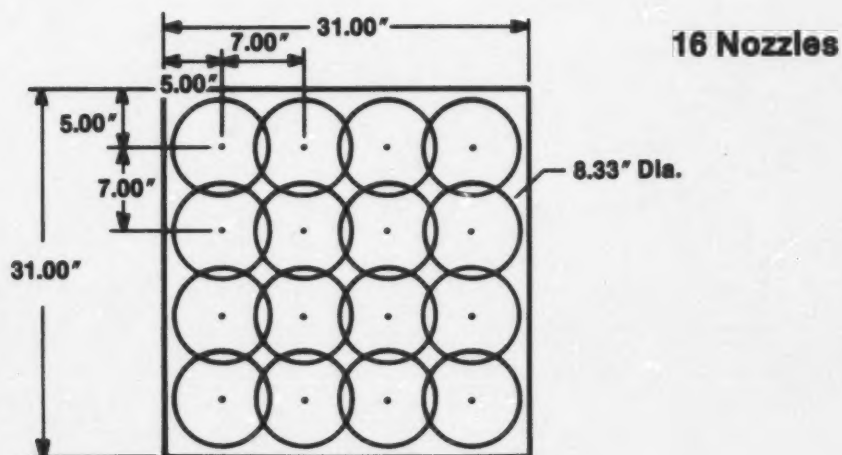
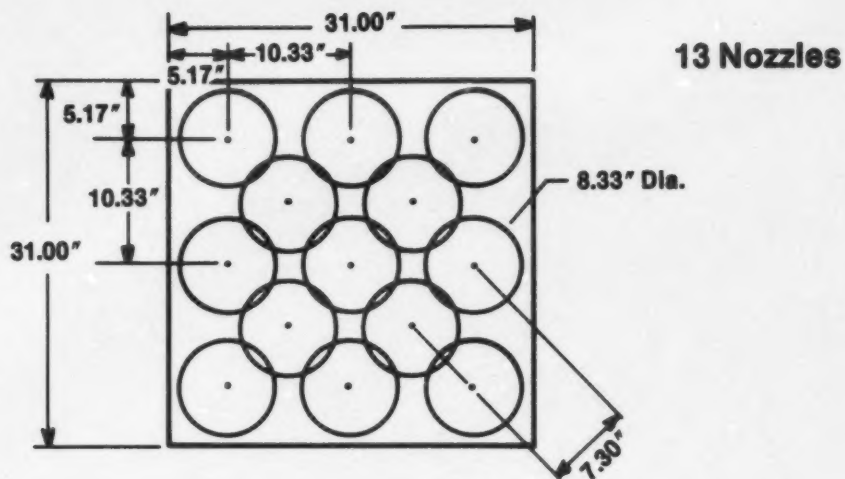
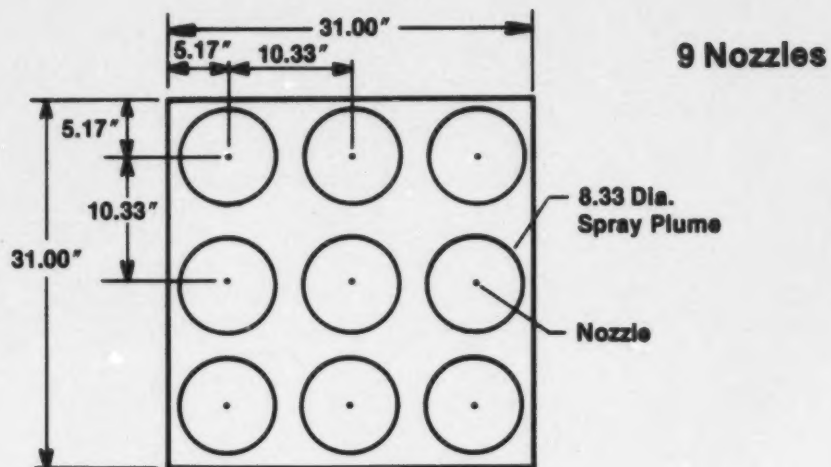


Figure 11. Nozzle Layouts and Location of the Cylindrical Humidification Zones for Each Nozzle. Base Tests at 14 ft/sec Flue Gas Velocity.

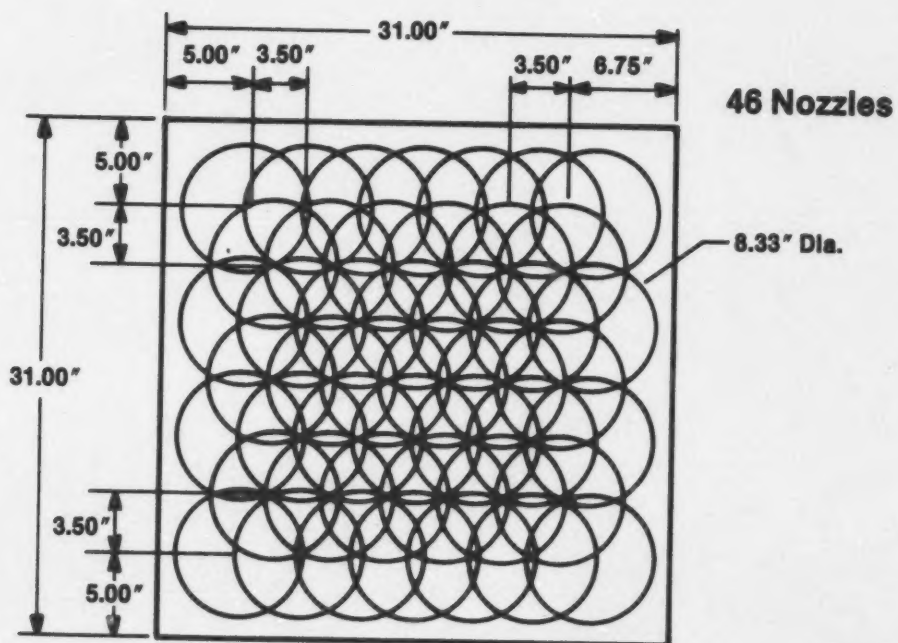
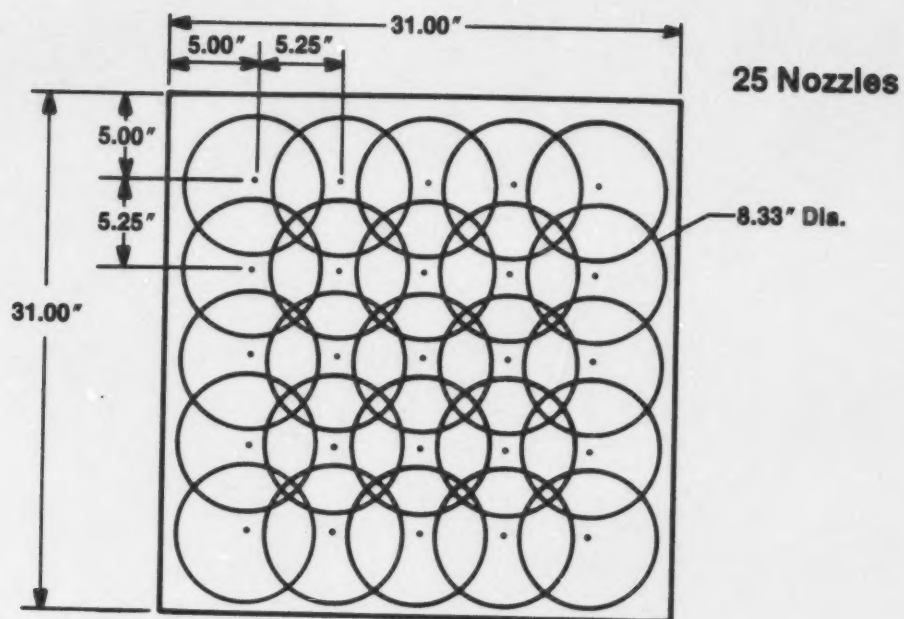


Figure 12. Nozzle Plume Overlap in Tests with 25 and 46 Nozzles.

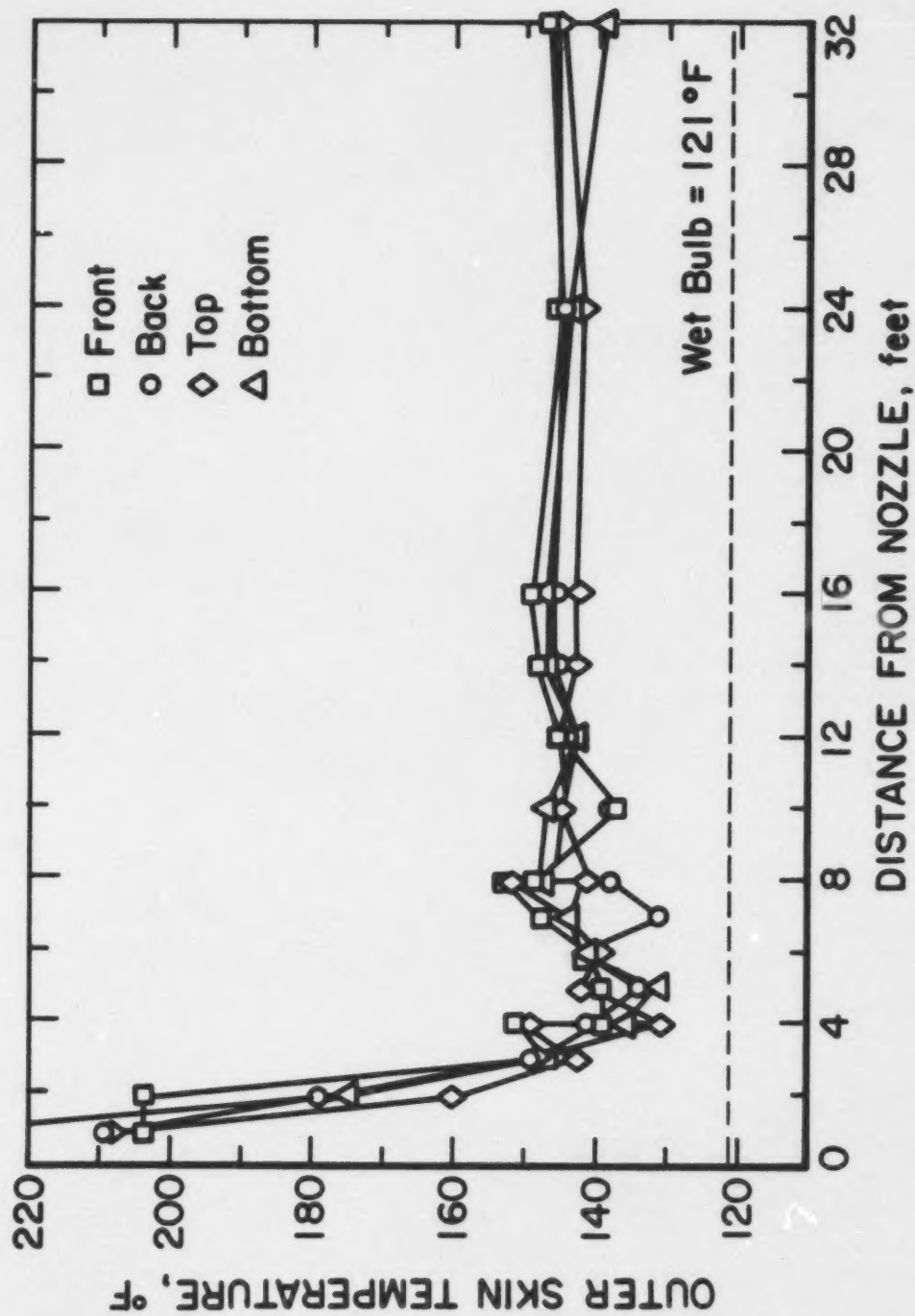


Figure 13. Duct Skin Temperature Profile in 25-Nozzle Test at 22°F Approach.

Figure 14. Total Residence Time as a Function of Boiler Load.

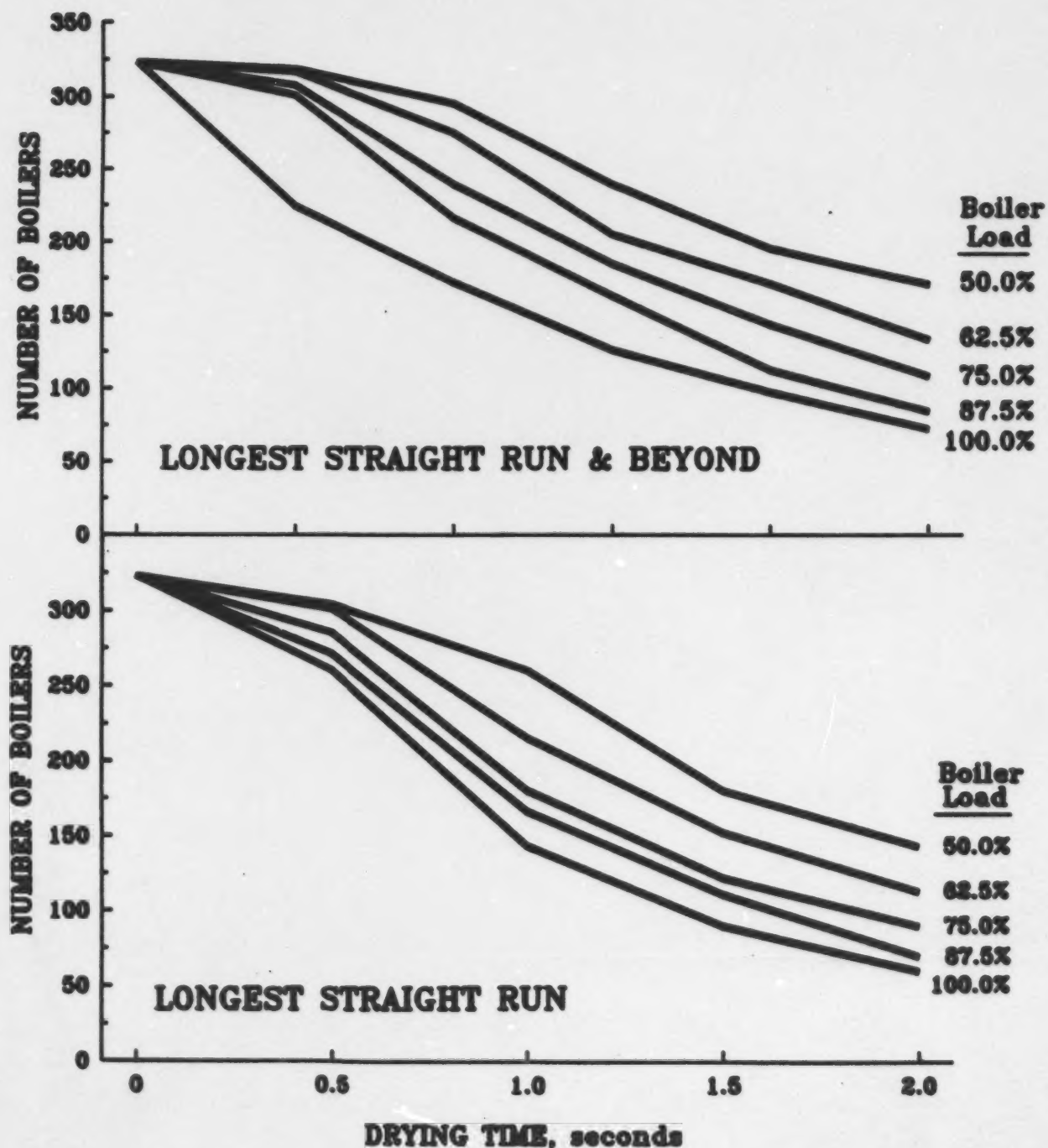


Table 1. SOLIDS LEACHATE ANALYSIS
5 MWe DOE-HALT Toronto Pilot Plant

Lab Report

SAMPLE NUMBER SOURCE	CONCENTRATIONS (mg/L)											Maximum Concentration Allowed Under RCRA
	50 Baghouse	51 Baghouse	155 Baghouse	197 ESP	234 Baghouse	236 Baghouse	238 ESP	245 Baghouse	296 Baghouse	306 ESP	311 ESP	
ARSENIC	0.0840	0.0600	<0.0020	0.0060	0.0030	0.0200	0.0060	< 0.0020	< 0.0020	0.0060	<0.0020	5.0
BARIUM	1.0000	0.3000	4.6000	5.6000	3.2000	4.5000	4.4000	2.7000	2.7000	3.300	4.5000	100
CADMIUM	0.0230	0.0130	<0.0050	<0.0050	< 0.0050	< 0.0050	<0.0050	< 0.0050	< 0.0050	<0.0050	<0.0050	1.0
CHROMIUM	0.0800	0.0600	0.0500	0.0500	0.0600	0.0600	0.0600	0.0500	0.0500	0.0600	0.0600	5.0
LEAD	0.0500	< 0.0300	0.0500	0.0500	< 0.0300	< 0.0300	0.0500	0.0800	< 0.0300	0.0400	<0.0300	5.0
MERCURY	0.0002	< 0.0002	<0.0002	<0.0002	0.0004	< 0.0002	0.0006	< 0.0002	< 0.0002	<0.0002	<0.0002	0.2
SELENIUM	0.0050	< 0.0040	<0.0040	<0.0040	0.0060	0.0600	0.0040	< 0.0040	0.0060	<0.0040	<0.0040	1.0
SILVER	0.0100	0.0100	0.0400	0.0400	0.0400	0.0400	0.0500	0.0400	0.0400	0.0500	0.0400	5.0

Table 2. COST ANALYSIS OF HALT PROCESS

Cost Component	First Year Costs		
	180 MW		500 MW
	Low Estimate	High Estimate	
Variable Operating Cost (mills/Kwh)	3.85	3.85	3.86
Fixed O&M (mills/Kwh)	0.64	0.82	0.57
Total Capital Required (million \$)	7.4	11.1	17.9
Gross Capital Require- ment (\$/Kw)	41.1	61.6	35.8
Capital Recovery Cost (mills/Kwh)	1.10	1.65	0.96
Total First Year Cost (mills/Kwh)	5.59	6.32	5.39
\$/Ton SO ₂ Removed	432	488	417

Table 3. DOE-IDS PRECIPITATOR - STATION I

FLUE GAS FLOW (acfm) @ 328°F	FLY ASH(1) (gr/acf)	LIME(2) PRODUCTS (gr/acf)	AVERAGE TEMPERATURE (°F)	NOMINAL SCA ft ² / 1000 acfm	RELATIVE OPACITY (%)
48,900	3.9	0	302	180	10.1
45,700	3.9	0	284	360	2.6
24,300	3.9	0	282	360	4.9
26,000	3.9	1.4	258	360	5.5
24,600	3.9	1.6	258	360	6.6
25,000	3.9	3.0	232	360	5.5
26,700	3.9	4.1	204	360	14.6
28,200	3.9	3.9	189	540	4.0
24,800	3.9	4.4	186	720	3.0

(1) Estimated

(2) Calculated based on average mol. wt. = 111

Table 4. OPERATING CONDITIONS FOR INDIVIDUAL J12 NOZZLES

Atomizing Air

Pressure	95 - 110 psig
Flow	2.9 - 3.3 scfm
Air/H ₂ O	45 - 55 scf/gal

Water

Pressure	ca. 85 psig
Flow	3.8 - 4 gal/hr

<u>Minimum Nozzle-Wall Spacing</u>	5 inches
------------------------------------	----------

Table 5. DRYING TIME DATA

<u>Number Of Nozzles</u>	<u>Approach to the Adiabatic Saturation Temperature of</u>	<u>Atomizing Air</u>		<u>Estimated Drying Time, sec</u>
		<u>psig</u>	<u>scf/gal</u>	
9	70	105	-	0.6
13	40-45	110	-	0.7
16	25-35	109	52	≤0.8
25	20-25	107	48	0.8
46	20-25	101	48	>1.2

Table 6. DUCT SURVEY RESPONSES

<u>Key Items</u>	<u>Number Targeted</u>	<u>Number Responded</u>	<u>Percent Response</u>
Utility Companies	85	55	64.7
Power Plants	181	125	69.1
Boiler Units	484	340*	70.2
Net Generating Capacity (MW)	120,411	87,231	72.4

*Includes 16 units equipped with hot-side ESP's

Table 7. CROSS-SECTIONAL DUCT AREA

<u>Area</u>	<u>Number of Units</u>	<u>Unit Percent</u>	<u>Megawatts</u>	<u>Megawatt Percent</u>
21-99 sq ft	102	31.5	9,658	11.6
100-299 sq ft	145	44.8	31,349	37.4
300-499 sq ft	54	16.7	28,838	34.4
500-2000 sq ft	<u>23</u>	<u>7.0</u>	<u>13,904</u>	<u>16.6</u>
	324	100.0	83,749	100.0

Average Value: 218.11 sq ft

Table 8. TOTAL RUN LENGTH

<u>Length</u>	<u>Number of Units</u>	<u>Unit Percent</u>	<u>Megawatts</u>	<u>Megawatt Percent</u>
5-99 ft	204	63.0	45,990	54.9
100-199 ft	53	16.4	15,662	18.7
200-299 ft	23	7.1	7,289	8.7
300-753 ft	<u>44</u>	<u>13.5</u>	<u>14,808</u>	<u>17.7</u>
	324	100.0	83,749	100.0

Average Value: 128.50 ft

Table 9. SUPERFICIAL GAS VELOCITY*

<u>Velocity</u>	<u>Number of Units</u>	<u>Unit Percent</u>	<u>Megawatts</u>	<u>Megawatt Percent</u>
5-29 ft/sec	55	17.0	10,215	12.2
30-49 ft/sec	119	36.7	26,642	31.8
50-69 ft/sec	116	35.8	37,454	44.7
70-92 ft/sec	<u>34</u>	<u>10.5</u>	<u>9,438</u>	<u>11.3</u>
	324	100.0	83,749	100.0

Average Value: 47.23 ft/sec

*100% Load through longest straight run.

Table 10. LONGEST STRAIGHT RUN

<u>Length</u>	<u>Number of Units</u>	<u>Unit Percent</u>	<u>Megawatts</u>	<u>Megawatt Percent</u>
5-39 ft	175	54.0	42,452	50.7
40-99 ft	103	31.8	26,735	31.9
100-149 ft	26	8.0	6,857	8.2
150-315 ft	20	6.2	7,705	9.2
	324	100.0	83,749	100.0

Average value: 53.74 ft

Table 11. DISTANCE FROM LONGEST STRAIGHT RUN TO PARTICULATE COLLECTOR

<u>Feet to PC</u>	<u>Number of Units</u>	<u>Unit Percent</u>	<u>Megawatts</u>	<u>Megawatt Percent</u>
0 ft	66	20.2	13,854	16.5
1-19 ft	142	43.6	31,910	38.1
20-49 ft	66	20.6	17,319	20.7
50-250 ft	50	15.6	20,666	24.7
	324	100.0	83,749	100.0

Average value: 27.29 ft

Table 12. GLOBAL APPROACH FOR ENHANCED MASS TRANSFER EFFECTS

- o Award to Energy and Environmental Research Corporation (Project Duration - 24 months beginning June 30, 1988)
- o Task Structure
 - o Task 1. Project Definition
 - Management Plan
 - Comprehensive Literature Review
 - o Task 2. Determination of Mass Transfer Effects
 - Gas and Liquid Phase Mass Transfer
 - Intrinsic Reaction Kinetics
 - Mathematical Model and Computer Code
 - Verification of Model
 - o Task 3. Development of Novel Techniques
 - Techniques to Improve Rate-Limiting Step
 - Single Drop Reactor/Duct Simulator Tests

Table 13. FUNDAMENTAL APPROACH FOR ENHANCED MASS TRANSFER EFFECTS

- o Award to Acurex, Inc. (Project Duration - 36 months beginning June 23, 1988)
- o Teaming - University of Texas at Austin
- o Task Structure
 - o Task 1. Project Definition
 - o Task 2. Mass Transfer Experimental Testing
 - Gas Film Mass Transfer
 - Liquid Film Mass Transfer
 - Sorbent Dissolution Effects
 - o Task 3. Computer Modeling
 - Fundamental Approach
 - Verification in 50-acfm Test Facility
 - o Task 4. Novel Technique Development
 - Sorbent Modification
 - Calcium Silicate-Based Sorbents
 - Tests at Various Scales

Table 14. FUNDAMENTAL INVESTIGATIONS OF DUCT AND ESP PHENOMENA

- o Award to Radian, Inc. (Project Duration - 28 months beginning September 27, 1988)
- o Teaming - Stone and Webster, Fossil Energy Research Corporation, ADA Technologies, Inc., Cham of North America, University of California at Irvine
- o Task Structure
 - o Task 1. Project Definition
 - Management Plan
 - Comprehensive Literature Review
 - o Task 2. Experimental Testing
 - Unit Construction and Shakedown
 - Parametric Tests
 - Evaluation of Sorbent/Fly Ash Recycle
 - Cleanability of Wall Deposits
 - Flow Visualization
 - ESP Testing
 - ESP Upgrading Techniques
 - o Task 3. Mathematical Model Development
 - First-Generation Duct Model
 - Duct Deposition Model
 - First-Generation ESP Model
 - ESP-Duct Dynamics Study

Table 15. SCALE-UP TESTS AND SUPPORTING RESEARCH

- o Award to Gilbert Commonwealth, Inc. (Project Duration - 38.5 months beginning September 23, 1988)
- o Teaming - Southern Research Institute
- o Task Structure
 - o Task 1. Project Definition
 - Management Plan
 - Comprehensive Literature Review
 - o Task 2. Modification of Test Unit
 - Unit Modifications
 - Advanced Diagnostic Techniques
 - o Task 3. Mathematical Model Development
 - Base-line Characterizations
 - Parametric Tests
 - Scale-up Data Obtained
 - Advanced Configuration Tests
 - Process Control
 - Failure Modes
 - o Task 4. Mathematical Model Validation
 - First-Generation Model Tests
 - Second-Generation Model Tests

Table 16. DUCT INJECTION TECHNOLOGY PROTOTYPE DEVELOPMENT

- o Award to United Engineers and Constructors, Inc. (Project Duration - 44 months beginning September 29, 1988)
- o Teaming - Babcock and Wilcox
- o Task Structure
 - o Task 1. Project Definition
 - o Task 2. Development of Engineering Design Criteria
 - Analysis of Existing Data
 - Model Validation Methodology
 - Scale-up Methodology and Prototype Design
 - Process Evaluations
 - o Task 3. Mathematical Process Model Development
 - Second-Generation Predictive Mathematical Model
 - Documentation of Model Protocol
 - Model Validation
 - o Task 4. Supporting Experimental Research
 - Nozzle Development
 - Waste Characterization
 - Supporting Studies
 - o Task 5. Technology Transfer
 - Duct Injection Working Group
 - Duct Injection Newsletter

Table 17. TOPICAL REPORTS TO BE PUBLISHED UNDER
THE DUCT INJECTION TECHNOLOGY DEVELOPMENT PROGRAM

Fundamental Investigation of Duct and ESP Phenomena

- Topical Report No. 1 - Literature Review and Annotated Bibliography
- Topical Report No. 2 - Parametric Evaluation of Process Performance
- Topical Report No. 3 - Evaluation of Sorbent/Fly Ash Recycle, and Cleanability of Wall Deposits
- Topical Report No. 4 - Flow Visualization Studies
- Topical Report No. 5 - Pilot-Scale ESP Testing
- Topical Report No. 6 - ESP Upgrading Strategies
- Topical Report No. 7 - Mathematical Modeling of the Duct Injection Process and ESP Performance
- Topical Report No. 8 - Modeling Duct Deposition Phenomena
- Topical Report No. 9 - Analytical Study of ESP - Duct Dynamics

Scale-Up Tests and Supporting Research

- Topical Report No. 1 - Literature Review and Annotated Bibliography
- Topical Report No. 2 - Evaluation of System Performance
- Topical Report No. 3 - Evaluation of Scale-up and Design Criteria
- Topical Report No. 4 - Testing of Advanced Configurations
- Topical Report No. 5 - Design and Testing of a Process Control System
- Topical Report No. 6 - Evaluation of Failure Modes
- Topical Report No. 7 - Testing of First-Generation Mathematical Model Predictions
- Topical Report No. 8 - Testing of Second-Generation Mathematical Model Predictions

Duct Injection Technology Prototype Development

- Topical Report No. 1 - Project Work Plan
- Topical Report No. 2 - Evaluation of Engineering Data
- Topical Report No. 3 - Methodology for Process Model Validation
- Topical Report No. 4 - Scale-Up Methodology and Prototype Design
- Topical Report No. 5 - Process Evaluations
- Topical Report No. 6 - Duct Injection Process and ESP Performance Model,
and Documentation of Modeling Protocol
- Topical Report No. 7 - Second-Generation Process Model Predictions
- Topical Report No. 8 - Prototype Nozzle Development
- Topical Report No. 9 - Duct Injection Process Waste Characterization
- Topical Report No. 10 - Supporting Experimental Studies

TECHNICAL AND ECONOMIC EVALUATION OF HYPAS

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ABSTRACT

HYPAS is a calcium-based dry injection retrofittable process for control of SO₂ and particulate matter emissions from coal-fired power plants. The HYPAS process is comprised of four basic steps which occur sequentially in the flue gas flow stream: (1) Fly ash removal by an existing precipitator; (2) Evaporative cooling to 10-20°F above the flue gas saturation temperature for water; (3) Dry alkali injection for reacting with SO₂ and SO₃; and (4) Collection of the desulfurization by-products and trace amounts of coal fly ash. HYPAS offers the advantages of separate and relatively pure solid wastes (i.e., fly ash and calcium by-products); evaporative cooling in a particulate-free environment which permits lower temperature operation without fouling internal duct surfaces, higher alkali utilization for SO₂ removal due to lower temperature operation and the use of a fabric filter, and an invisible plume due to high collection efficiency of particulate matter and SO₃.

In 1986, the Electric Power Research Institute (EPRI) conducted proof-of- concept testing of HYPAS at a 1000 scfm pilot plant at the Arapahoe Test Facility in Denver. Based upon favorable results, a new 4 MW-scale HYPAS pilot plant was designed and installed at EPRI's High Sulfur Test Center in New York. A one-year test program is being implemented to confirm the SO₂ removal capability for the process, and to develop engineering guidelines for optimizing and scaling-up

HYPAS for full-scale installations. Results from the 1000 scfm pilot plant will be summarized in this paper.

HYPAS and conventional wet FGD designs and cost estimates were prepared for three utility power plant scenarios in parallel with the 4 MW pilot plant testing. Each scenario represents a different design class of retrofit application and was based on an actual power plant design and equipment configuration. Performing these analyses for actual plants, and not hypothetical plants, provided significant insights regarding the specific design problems associated with retrofitting these processes. The power plant designs are: (1) Coal-fired boiler equipped with an underperforming cold-side precipitator; (2) Coal-fired boiler equipped with two precipitators in series, in this instance the second precipitator is converted to a pulse-jet fabric filter; and (3) Coal-fired boiler equipped with two precipitators in parallel, in this instance one precipitator is converted to a pulse-jet fabric filter and located downstream of the other. In all three cases, the capital and O&M costs for HYPAS were compared to those for wet FGD. HYPAS capital costs were approximately one-third of those for FGD and the total levelized costs (for 20 years) were approximately 45% of those for FGD.

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INTRODUCTION

A variety of retrofittable SO₂ control technologies will be necessary to accommodate the range of power plant types, fuels, and reduction requirements which the electric power industry will have to retrofit under acid rain legislation being considered by the U.S. Congress. Depending upon the regulatory scenario, for individual units the SO₂ emissions reduction requirements may span from 30 to 90%. In recognition of this legislative activity, a goal of EPRI has been to develop retrofittable dry systems which circumvent to the maximum degree practical, the complexity and high cost of conventional wet flue gas desulfurization processes (FGD). Direct injection processes, such as furnace sorbent injection or economizer injection, are attractive because of their simplicity and minimum capital cost. However, these processes may be limited by moderate SO₂ removal capability, adverse impacts on the electrostatic precipitator (ESP) used for particulate matter collection, boiler convection pass fouling, ductwork fouling if humidification is utilized for ESP enhancement, and waste management problems. HYPAS is a new process with performance that is not significantly constrained by these considerations.

In 1986, EPRI sponsored proof-of-concept testing of HYPAS at 1000 scfm scale at the EPRI Arapahoe Test Facility in Denver. Based upon favorable results, a new 4 MW-scale HYPAS pilot plant was designed and installed at EPRI's High Sulfur Test Center in New York. A one-year test program is being implemented to confirm the SO₂ removal capability for the process, and to develop engineering guidelines for optimizing and scaling-up HYPAS for full-scale installations. In parallel with the pilot-scale test program, conceptual designs and cost estimates are being prepared for typical full-scale installations of HYPAS. This paper summarizes the results to date from these collective efforts.

HYPAS PROCESS DESCRIPTION

HYPAS is a retrofittable process for control of SO₂ and particulate matter (PM) emissions from coal-fired power plants. HYPAS entails the addition of a fabric filter as a second PM collection device, such as a pulse jet, located downstream of the existing electrostatic precipitator (ESP). As illustrated in Figure 1, the principal HYPAS equipment components are: a new fabric filter for collection of SO₂ by-products and trace amounts of fly ash which pass through the old ESP; a means for reducing the flue gas temperature and raising the relative humidity entering the

fabric filter (e.g., evaporative cooling or heat exchange); and a dry sorbent injection subsystem. A pulse-jet fabric filter is preferred because it is the most efficient collector per unit of volume and plan area for any PM device. Moreover, in instances where there are two existing ESPs, one may be converted to a pulse-jet utilizing the ESP foundations, structural supports, and casings. Flue gas cooling will in most instances be accomplished using direct injection of water immediately downstream of the ESP and prior to the injection of dry sorbent. The HYPAS process has a number of distinct advantages over other dry and wet FGD processes:

1. Two solid waste streams are produced: fly ash and calcium-based SO₂ by-products. The pre-existing management scheme for fly ash disposal, use, or sale is not impacted. The relatively pure SO₂ by-products may be more easily disposed or converted to a usable product.
2. Many older power plants have ESPs with marginal performance which will require significant upgrading if the unit is retrofit with conventional FGD or operation with lower sulfur coal is desired. The addition of the pulse-jet fabric filter at the end of the process flow path will assure very high overall PM collection efficiency.
3. Performing the flue gas cooling/humidification step in an ash-free environment will permit cooling to lower temperatures (i.e., closer approach to water saturation temperature of approximately 130 to 140 F) without causing significant fouling or deposition on the internal surfaces of the flue gas ductwork. Hence, the pulse-jet fabric filter will operate at closer approach temperatures, sorbent utilization will be greater, and SO₂ removal will be higher than for other dry processes operating at equivalent Ca/S ratios.
4. Because the HYPAS process equipment is located between the existing ESP and the stack, there is minimal impact on operation and performance of the existing boiler system.
5. The dust cake containing calcium sorbent that has not fully reacted while suspended in the flue gas results in further reaction with SO₂, higher calcium utilization, and higher overall SO₂ removal.

PROOF-OF-CONCEPT TESTING

TEST CONFIGURATION

Testing of the HYPAS process was conducted utilizing a 1000 scfm pilot plant at EPRI's Arapahoe Test Facility in Denver (Ref 1). The work primarily addressed the SO₂ removal potential for the process. Figure 2 is a schematic of the HYPAS pilot plant at Arapahoe. For convenience, a mechanical shaker baghouse was used rather than a pulse jet which is viewed to be the optimum baghouse type for retrofit applications. The flue gas was supplied to the pilot plant from an adjacent utility boiler firing low-sulfur coal. Flue gas entering the pilot plant was spiked with SO₂ to concentrations up to 3000 ppm and then passed through a 3-field ESP for fly ash removal. The gas was then cooled via in-duct humidification using air-atomized water nozzles. Dry calcium-based sorbents were then injected into the cooled flow stream, upstream of the baghouse. SO₂, O₂, and NO concentrations in the gas stream were continuously monitored at the pilot plant inlet and outlet.

PARAMETRIC EFFECTS ON SO₂ REMOVAL

In general, no significant differences are present in the SO₂ process chemistry between HYPAS and other dry injection schemes. Thus, the process parameters that are important for direct injection are also important for HYPAS. Among these, the two that influence SO₂ removal to a major degree are Ca/S ratio and the approach to water saturation temperature (ΔT_{sat}). The effect of approach temperature is shown in Figure 3 (Refs 5 and 6) for injection of hydrated lime, Ca(OH)₂ at Ca/S = 2. SO₂ removal is fairly low until the approach temperature is 40 F or less. At an approach temperature of 10 F the SO₂ removal was approximately 80%. The effect of Ca/S ratio on SO₂ removal is shown in Figure 4. This particular test series was conducted with steam and water being injected for evaporative cooling to ΔT_{sat} = 20 F. Steam was one variable investigated (on limited basis) for increasing SO₂ removal. It was found to be marginally beneficial under certain conditions. The SO₂ removal increased as the amount of calcium increased. During these tests a measurement was made of the SO₂ removal which occurs while the sorbent particles are in suspension versus while the sorbent is deposited in the dust cake on the filter bags. It was found that about half of the SO₂ removal occurs in suspension and about half by the dust cake. Of that which occurs in suspension, most of the reactions are complete within the first second following injection.

Beside ΔT_{sat} and Ca/S ratio, several other parameters were briefly investigated. Different sorbents were tested, including: various commercial sources of Ca(OH)_2 ; high surface Ca(OH)_2 produced by alcohol hydration; Ca(OH)_2 with additives (e.g., surfactants, sodium, chloride), and an "EPA-supplied" sorbent which is a mixture of fly ash and Ca(OH)_2 . Essentially, little or no difference was observed in SO_2 removal for any of these sorbents in the HYPAS process when supplemental steam injection was not used. Similarly, initial SO_2 concentrations were varied from 900 to 3000 ppm, and no differences in SO_2 removal was observed for a constant Ca/S ratio and ΔT_{sat} .

One of the attractive features of HYPAS is the separation of fly ash and calcium by-products, which may facilitate recycling (in terms of the quantity of mass to be handled) of the reaction by-products ("recycle") for enhanced SO_2 removal. Limited testing in which only recycle and recycle in combination with fresh sorbent were injected showed that the reaction by-products were essentially unreactive although they contain unutilized calcium corresponding to $\text{Ca/S} \gg 2$. This observation suggests that the hydrated lime particles reacted with SO_2 until a sulfate layer builds on the particle surface creating a diffusion limit that prevented further reaction. Moreover, this result suggests that recycle processing (e.g., grinding) will increase the reactivity of the material prior to injection. Further testing will be conducted at the 4 MW pilot plant to quantify the effectiveness of recycle and measure the benefit of recycle grinding.

DUCT DEPOSITION

One of the concerns with dry injection technologies, particularly when implemented in conjunction with flue gas humidification, is the potential for buildup of deposits on ductwork internal surfaces. In the Arapahoe pilot plant the ductwork diameters were small and not representative of full-scale systems in terms of wall area to flow area ratios. Nevertheless, a few observations were possible which support the claimed advantages of HYPAS. For example, at $\Delta T_{sat} = 20^\circ \text{F}$.

1. If sorbent was injected upstream of the humidification water sprays, Ca(OH)_2 /fly ash deposition would permit operation of the pilot plant for less than one hour before the test had to be terminated to clean-out the ductwork.

2. If sorbent was injected after humidification such that only fly ash interacted with the water sprays, operation for only 8 hours was possible before the deposits interfered with the experiments.
3. With HYPAS, no duct deposition occurred and steady state experiments could be conducted indefinitely without the problems discussed for the two cases above.

CONCLUSIONS FROM THE PROOF-OF-CONCEPT TESTING

The tests demonstrated SO₂ removals of 50-80% at approach temperatures of 20-10 F for a Ca/S = 2. The elimination of duct deposition problems by humidifying in an ash-free environment allowed continuous operation at approach temperatures below those possible with direct injection/humidification processes. The corresponding SO₂ removal will be higher for the same Ca/S ratio, or yield equivalent SO₂ removal at lower Ca/S ratios. In either instance, the cost effectiveness for the HYPAS process is significantly improved due to increased sorbent utilization.

COST ESTIMATES

The design and cost analyses were performed for actual units, in part, to identify important design considerations common to retrofitting the HYPAS process and develop increase confidence in the cost estimates. In each case, comparison costs were developed for wet FGD systems utilizing similar design and economic criteria and assumptions.

DESIGN SCENARIOS

HYPAS conception designs and cost estimates have been prepared for three coal-fired power plant scenarios. Each scenario represents a different design class of retrofit application and is based on an actual power plant design and equipment configuration. The case for retrofitting to a boiler with only one ESP is viewed to be the most likely candidate for HYPAS installation among the U.S. population of boilers. For each scenario, a "Base" configuration for HYPAS was designed and cost estimates prepared to $\pm 20\%$. For comparison purposes, the costs for retrofitting a

conventional wet limestone scrubber were estimated using EPRI's guidelines (Ref 2).

A. Coal-fired Boiler Equipped with and Underperforming Cold-side ESP

The subject unit for this scenario was Duke Power Company's Marshall Unit 1. This coal-fired unit is equipped with one cold-side ESP and would represent the most common retrofit application of HYPAS. As illustrated in Figure 5, a new pulse-jet fabric filter would be installed between the existing ESP and the induced draft fan. Humidification and sorbent injection equipment would be installed in the ductwork connecting the ESP and pulse-jet fabric filter.

B. Coal-fired Boiler Equipped with Two ESPs in Parallel

Duke Power Company's Marshall Unit 3 was the subject for this scenario. This unit presently has two ESPs in parallel as illustrated in Figure 6. In this instance, the study evaluated the application of HYPAS by reconfiguring the two ESPs into a series arrangement, and converting the downstream ESP to a pulse-jet fabric filter.

C. Coal-fired Boiler Equipped with Two ESPs in Series

Duke Power Company's Allen Unit 3 was the subject for this scenario. This unit presently has two ESPs in series (a hot-side followed by a cold-side) as shown in Figure 7. Retrofitting HYPAS encompassed reconfiguring the ductwork and conversion of the hot-side ESP to a pulse-jet fabric filter.

DESIGN CRITERIA

The economic analysis was performed in accordance with EPRI methodology (Refs 3 and 4). The major premises and assumptions that were used are summarized in Table 1 for the base cases. Several options (variations to the base cases) were also estimated and these conditions are summarized in Table 2.

DISCUSSION OF ECONOMIC RESULTS

The estimated costs for retrofitting FGD and HYPAS to each of the three coal-fired units is summarized in Table 3. All of the costs have been levelized for 20 years and are presented in mills/kWh. For comparison purposes, the FGD and

The cost impact for including recycle (with grinding prior to injection) at a recycle ratio equal to 5 (i.e., mass ratio of recycle to fresh sorbent) is illustrated by comparing the results for Option 3 to the base case for Marshall 1. Including recycle will increase the capital and variable O&M costs by 5 to 10%. There will also be a corresponding increase in SO₂ removal, but to date, that has not been addressed in this study.

The cost advantage for purchasing pebble lime and hydrating it on-site as compared to purchasing hydrated lime, is illustrated by comparing the base case to Option 4 for Marshall 1. It can be seen that the variable O&M cost increased by 30% and the total cost increased by 14% relative to the base case when hydrated sorbent is purchased.

Other Design Considerations

Performing the design study for actual units clarified several important design considerations that may not have surfaced had the study used hypothetical plants. First, installation of the pulse-jet fabric filter usually involves new connecting ductwork. The preferred layout is based on considerations of orientation and residence time requirements for humidification, and upon the existing locations of the ESP and induced draft fans. In many instances the pulse jet will be located above the existing ESP and the connecting ductwork will be vertically oriented. The inlet and outlet ductwork can be connected to the same end of a pulse jet and this versatility provides for more layout options.

Induced draft fan size and location are also important considerations. The pulse jet will add a few inches of pressure drop along the flow path, but because the gas is cooled and the volumetric flow rate at the fan is lower, it may or may not be necessary to upgrade the fans. For the Duke Power units, new fans will be needed for HYPAS at Marshall 1 and Allen 3; the existing fans are adequate for Marshall 3.

SUMMARY

HYPAS is a combined SO₂ and particulate matter emissions control process that is presently being developed under the joint sponsorship of EPRI, ESEERCO, Consolidated Edison of New York, Duke Power Company, and NYSERDA. Proof-of-concept testing at a 1000 scfm pilot plant has confirmed process performance in terms of SO₂ removal potential. Testing on a high sulfur coal pilot plant at 6500 scfm (4 MW) is underway at EPRI's High Sulfur Test Center near Buffalo, New York.

HYPAS base cases are all for 50% SO₂ removal. Typically, FGD systems would be designed for 70-90% SO₂ removal and HYPAS for 50-70% SO removal. In future studies (Phase 2), the FGD and HYPAS processes will be designed for their respective optimum conditions and the cost effectiveness will be compared on a levelized \$/ton of SO₂ removed over 20 years.

The total capital requirement for FGD systems ranged from 7.0 to 8.9 mills/kWh. By comparison, the capital requirement for HYPAS ranged from 2.3 to 3.4 mills/kWh, or about 35% of the cost of the FGD equipment. The capital cost can also be compared on a \$/kW basis as illustrated below.

	<u>Marshall 1</u>	<u>Marshall 3</u>	<u>Allen 3</u>
Rating (MW)	350	650	275
Wet FGD	262 \$/kW	239 \$/kW	305 \$/kW
HYPAS	105 \$/kW	79 \$/kW	114 \$/kW

Comparing the total costs for the base HYPAS cases to FGD illustrates a similar cost advantage, approximately two-to-one, for HYPAS when the systems are designed and operated for equivalent levels of SO₂ removal. This advantage will diminish (in terms of \$/ton SO₂ removed) if the FGD system is operated at 90% removal, capacity factors increase above 65%, or plant life is longer than 20 years. Conversely, the HYPAS advantage will increase for lower SO₂ removal requirements, capacity factors less than 65%, or plant life shorter than 20 years.

The HYPAS base cases were for an approach temperature of 20 F and corresponding SO₂ removal of 50% at a Ca/S = 2. If however, an approach temperature of 10 F can be achieved, then Ca/S can be lowered to 1, and still produce an equivalent amount of SO₂ removal. As shown in the Option 2 cases, the variable O&M costs would decrease by about 35% and the total cost would decrease by about 15%.

Designing HYPAS for 2.5% S coal as compared to 1.1% S coal results in 10% higher capital costs, 40% higher variable O&M costs, and 33% higher total costs. These relationships were essentially the same for both the Marshall 1 and Allen 5 units.

Work is underway at the 4 MW HYPAS pilot plant at EPRI's High Sulfur Test Center. Startup commenced in August 1988 with the commissioning of the pulse-jet fabric filter-- the first application of a pulse jet for collection of fly ash from a high sulfur coal-fired utility boiler. The preliminary results, in terms of collection efficiency and pressure drop have been very encouraging. At the time of the preparation of this paper, work continues to commission the humidification and alkali injection subsystems.

Preliminary results from the 1000 scfm tests indicate that HYPAS permits operation at approach temperatures below those normally associated with dry injection/humidification processes, and this will result in proportionally higher levels of alkali utilization. In addition, the HYPAS process offers the advantages of separate fly ash and by-product solid waste streams, and efficient collection of particulate matter.

Cost estimates have been prepared for retrofitting HYPAS to three coal-fired units in the Duke Power Company generating system. In all three cases, the levelized capital and O&M costs were compared to conventional wet limestone FGD systems for equivalent levels of SO₂ removal. HYPAS capital costs were approximately 35% of those for FGD in all three cases, and the total levelized costs (20 years) were approximately 45% of the those for FGD. Pending results from the 4 MW test program, the cost estimates will be updated and expanded.

ACKNOWLEDGEMENTS

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DISCLAIMER

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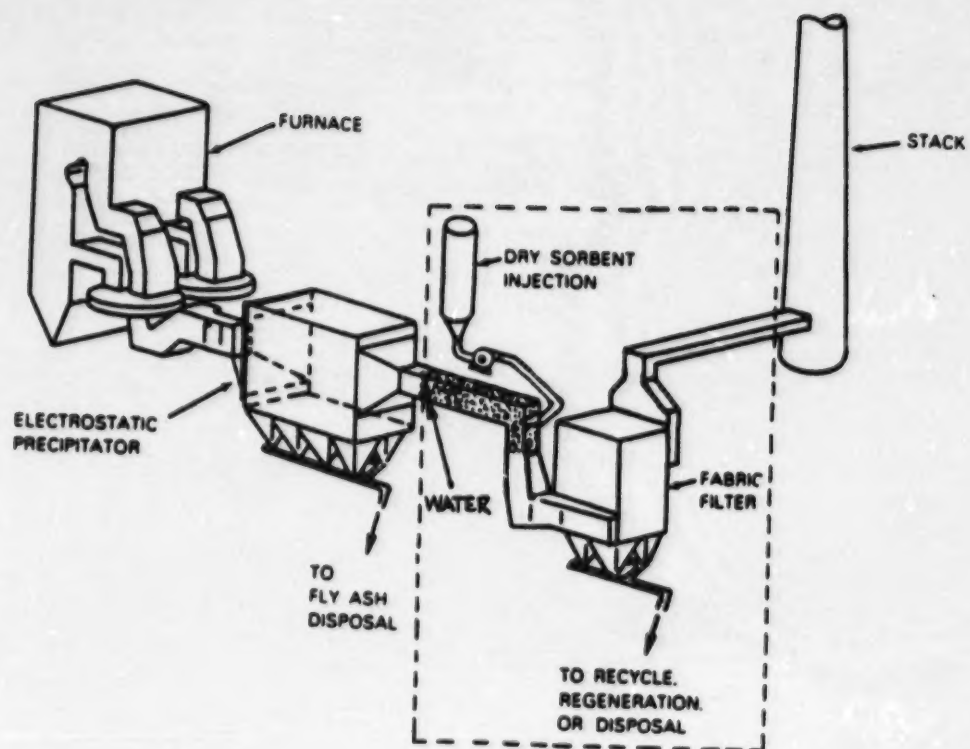


Figure1. HYPAS equipment components for retrofit to a coal-fired power plant.

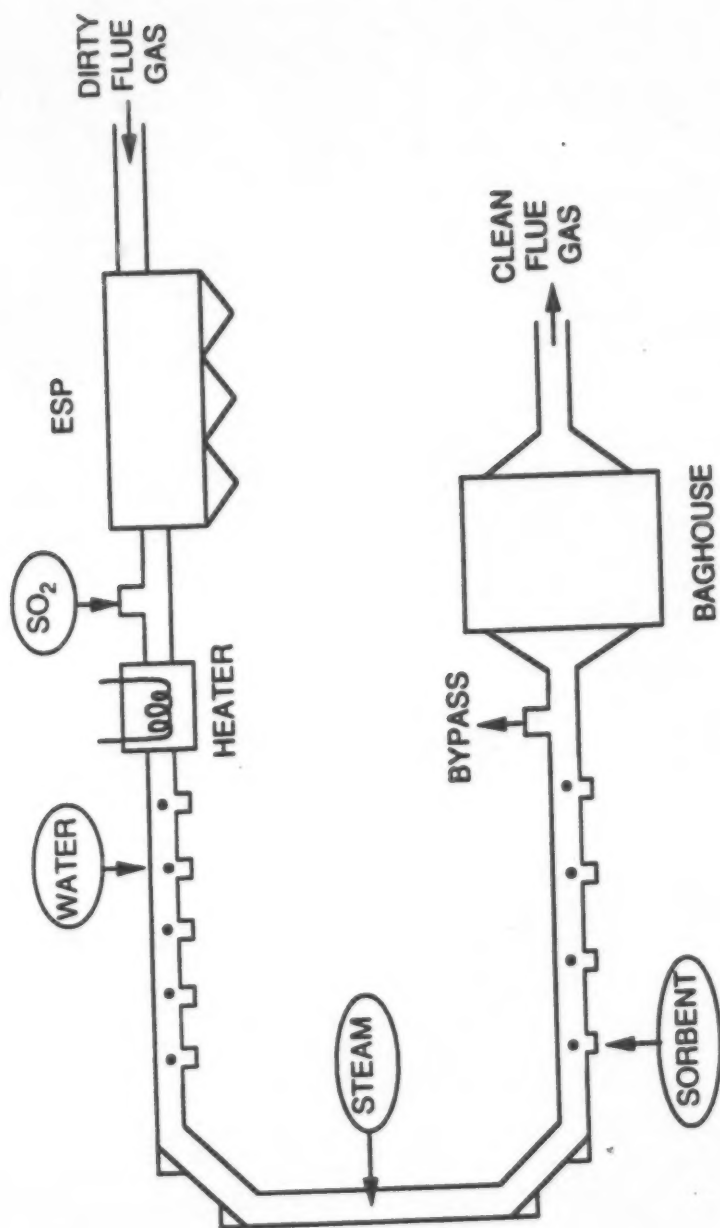


Figure 2. Schematic of HYPAS 1000 scfm pilot plant at EPRI's Arapahoe Test Facility

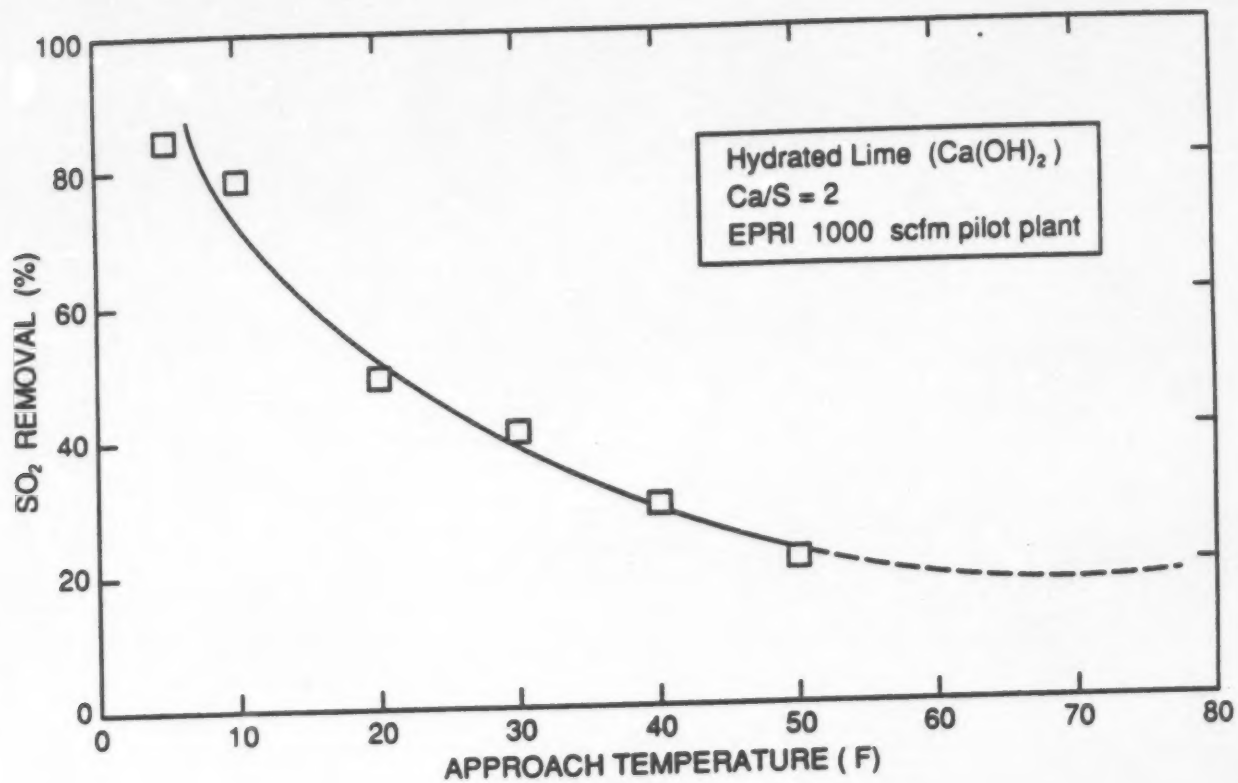


Figure 3.

Effect of approach temperature on
 SO_2 removal for HYPAS process.

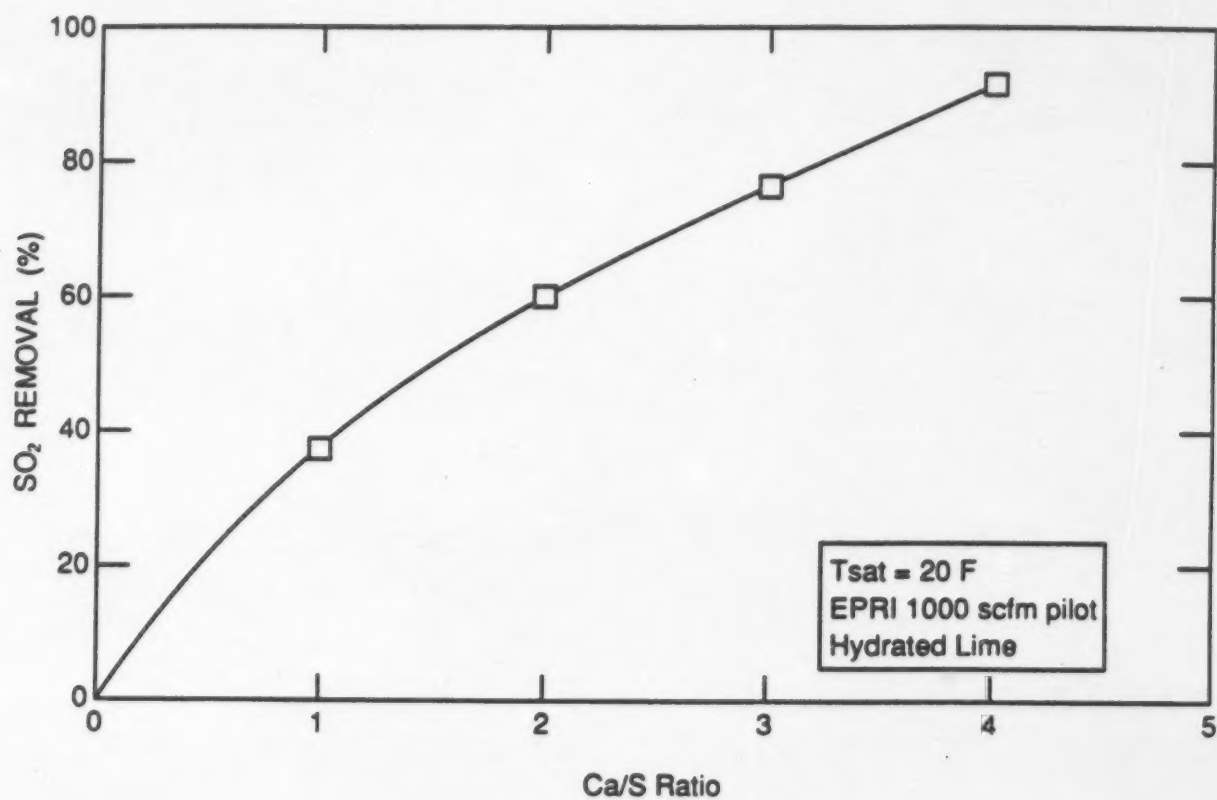


Figure 4.

Effect of Ca/S ratio on
SO₂ removal for HYPAS process.

Figure 5. Schematic of HYPAS conversion for Duke Power's Marshall 1.

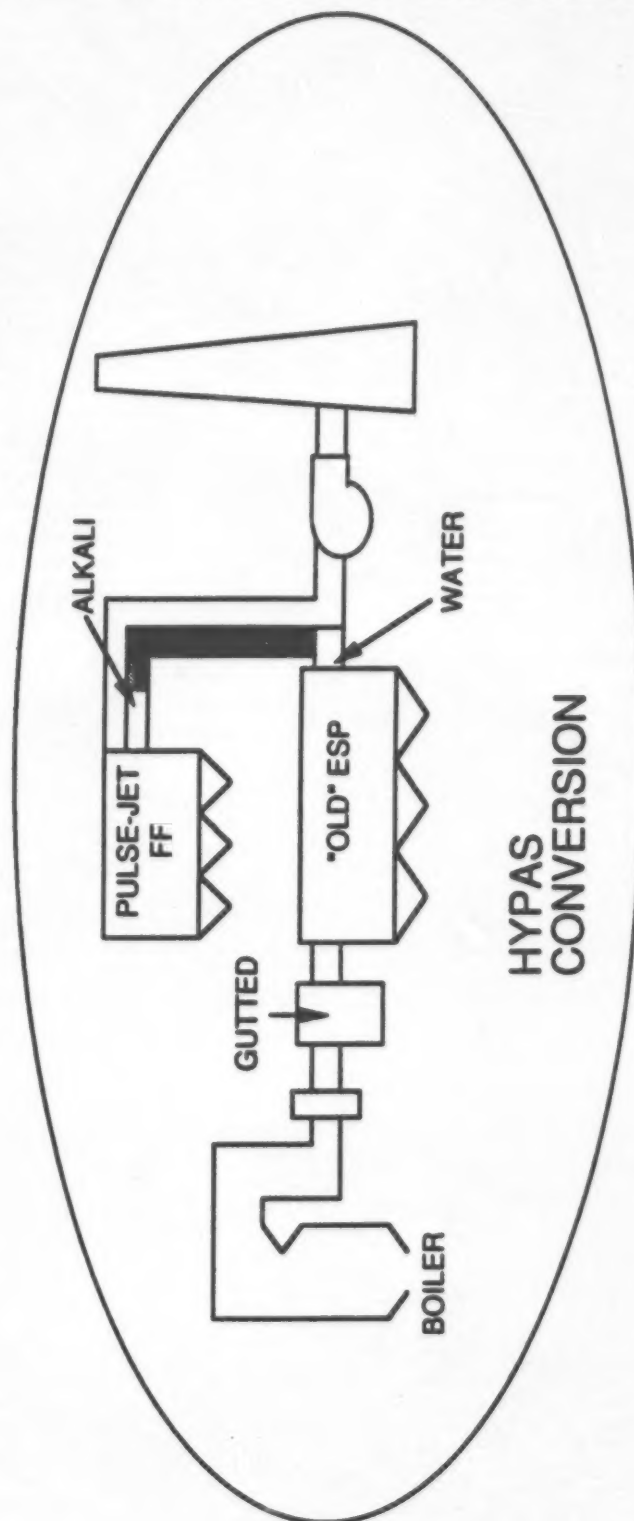
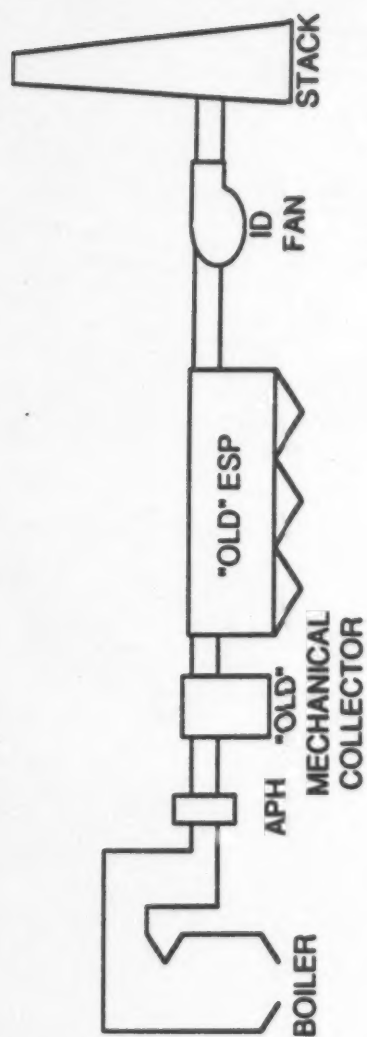


Figure 6. Schematic of HYPAS Conversion for Duke Power's Marshall 3

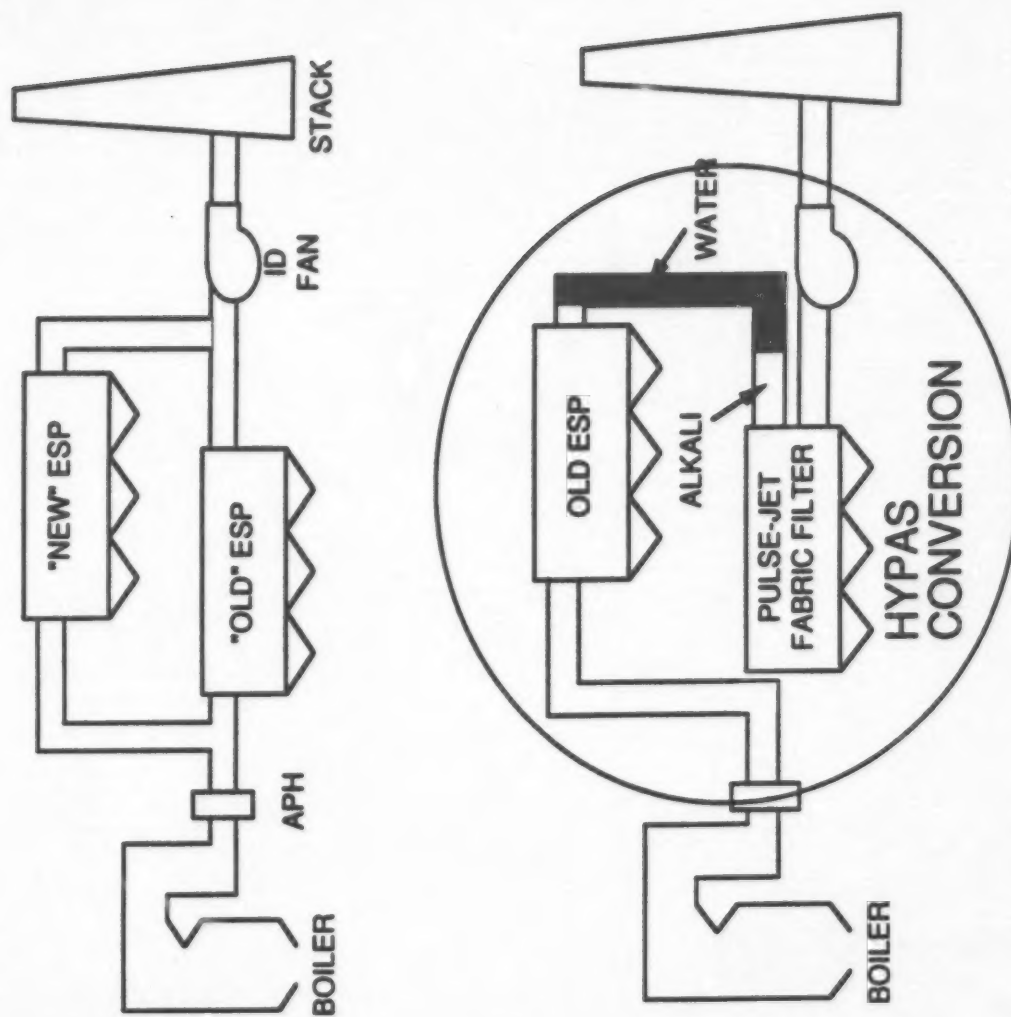


Figure 7. Schematic of HYPAS Conversion for Duke Powers' Allen 5

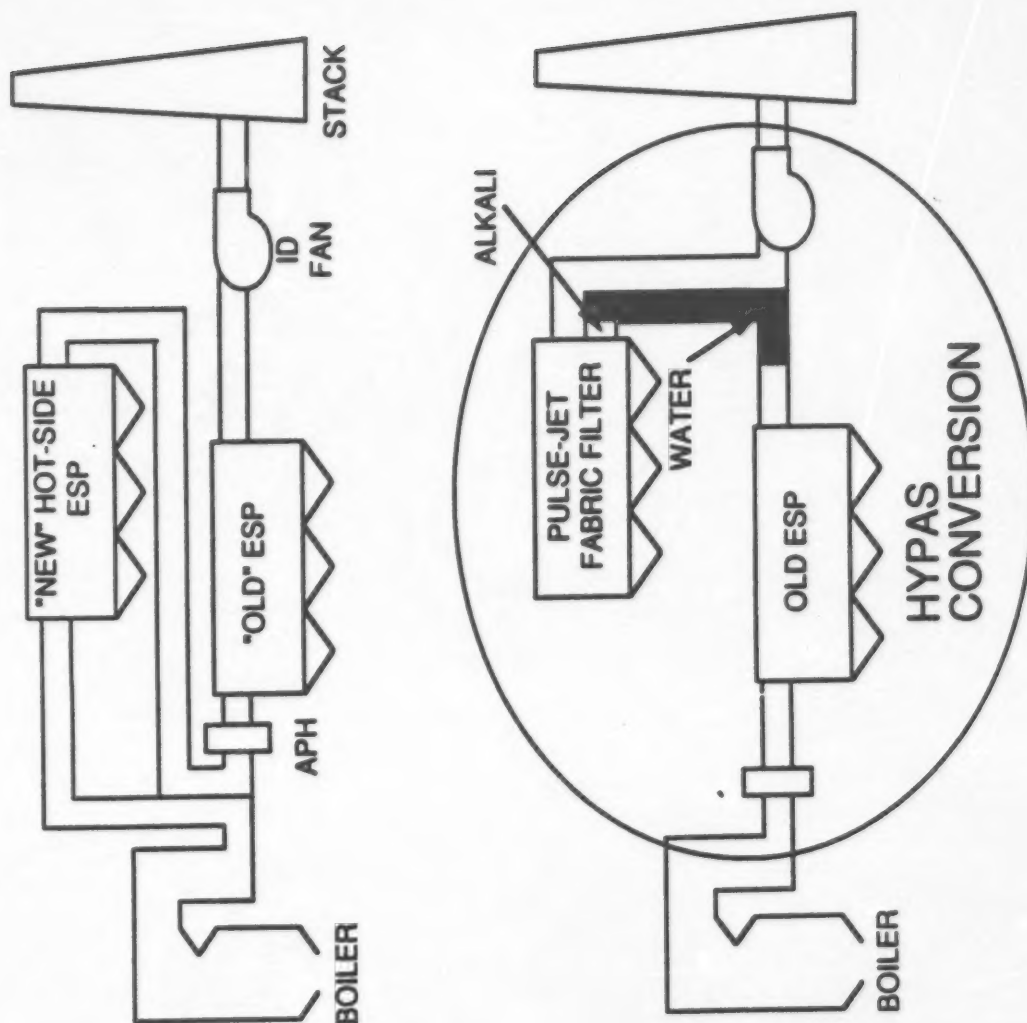


TABLE 1. DESIGN PREMISES FOR ECONOMIC EVALUATION OF HYPAS
- BASE CASES -

	<u>Marshall 1</u>	<u>Marshall 3</u>	<u>Allen 5</u>
Rating, MW	350	650	275
Capacity factor, %	65	65	65
Gas flow rate, acfm	1,233,000	2,140,000	1,128,000
Fuel sulfur, %	1.1	1.1	1.1
Fuel HHV, Btu/lb	11,000	11,000	11,000
SO ₂ removal, %	50	50	50
Ca/S	2	2	2
ΔT_{sat} , F	20	20	20
Purchased alkali	Pebble Lime	Pebble Lime	Pebble Lime
Alkali preparation	On-site Hydration	On-site Hydration	On-site Hydration
Pebble lime, \$/ton	75	75	75
Recycle	none	none	none
Recycle processing	none	none	none
Humidification	In-duct/water	In-duct/water	In-duct/water
Residence time, sec	>1	>1	>1
Fly ash disposal (1)	landfill/sell	landfill/sell	land fill/sell
SO ₂ by-product disp.	new landfill	new landfill	new landfill
Pulse-jet Baghouse	new	Convert ESP	Convert Hot ESP
SO ₃ Conditioning	eliminate	n/a	n/a
Levelizing period, yr	20	20	20
Year's dollars	1988	1988	198c4

(1) landfill/sell means that a portion of the fly ash is commercially sold.

TABLE 2. OPTIONAL CASES FOR HYPAS ECONOMIC ANALYSIS.

	<u>Option 1</u>	<u>Option 2</u>	<u>Option 3</u>	<u>Option 4</u>
Marshall 1	2.5% Fuel S	Ca/S = 1 $\Delta T_{\text{sat}} = 10 \text{ F}$ SO ₂ = 50%	w/Recycle	Purchase Ca(OH) ₂
Allen 3	2.5% Fuel S	Ca/S = 1 $\Delta T_{\text{sat}} = 10 \text{ F}$ SO ₂ = 50%		

TABLE 3. SUMMARY OF ESTIMATED COSTS FOR HYPAS AND CONVENTIONAL WET FGD FOR THREE COAL-FIRED POWER PLANT RETROFITS

(Levelized Busbar Costs, mills/kWh)			
	<u>Marshall 1</u>	<u>Marshall 3</u>	<u>Allen 3</u>
Wet FGD			
Capital	7.7	7.0	8.9
Fixed O&M	5.9	4.4	6.6
Variable O&M	<u>4.7</u>	<u>4.6</u>	<u>4.7</u>
TOTAL	18.3	16.0	20.2
HYPAS - BASE			
Capital	3.0	2.3	3.4
Fixed O&M	2.0	1.4	2.3
Variable O&M	<u>3.7</u>	<u>3.4</u>	<u>3.7</u>
TOTAL	8.7	7.1	9.4
HYPAS - OPTION 1			
Capital	3.3		3.8
Fixed O&M	2.1		2.4
Variable O&M	<u>6.2</u>		<u>6.2</u>
TOTAL	11.6		12.4
HYPAS - OPTION 2			
Capital	3.0		3.3
Fixed O&M	2.0		2.2
Variable O&M	<u>2.5</u>		<u>2.5</u>
TOTAL	7.5		8.0
HYPAS - OPTION 3			
Capital	3.5		
Fixed O&M	2.0		
Variable O&M	<u>3.9</u>		
TOTAL	9.4		
HYPAS - OPTION 4			
Capital	3.1		
Fixed O&M	2.0		
Variable O&M	<u>4.8</u>		
TOTAL	9.9		

**Title: OPERATING EXPERIENCE WITH A DRY FGD PLANT USING A
 CIRCULATING FLUID BED (CFB) AT THE LIGNITE-FIRED POWER
 STATION OF PREAG IN BORKEN, FEDERAL REPUBLIC OF GERMANY**

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DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Abstract:

At the end of 1987/beginning of 1988, a dry flue gas desulfurization plant was brought on stream at the BORKEN lignite-fired power station of PREAG. This plant operates on the expanded Circulating Fluid Bed (CFB) principle. It is designed to clean a flue gas flow of max. 620.000 m³ n/h (moist) laden with 10-25 g SO₂/m³ n and approx. 13 g fly ash/m³ n to a residual SO₂ content of < 400 mg/m³ n using Ca(OH)₂. The plant is operated at a reaction temperature of approx. 70°C, achieved by spraying water into the CFB absorber.

A newly installed and an existing electrostatic precipitator clean the flue gas down to < 50 mg dust/m³ n. The reaction product, a mixture of lignite fly ash, CaSO₃.1/2 H₂O, CaSO₄.1/2 H₂O, CaCO₃ and Ca(OH)₂, is transported to a worked-out openpit lignite mine which has been converted to a dump. This residue is mixed with water and sets to form a material which is more impermeable to water than clay and has a compression strength similar to lightweight concrete.

Since 1978 more than 20 plants are operating on this CFB system starting with a CFB dry gas cleaning for HF adsorption for aluminium electrolysis off gases, waste gases from glass works and HCl-, SO₂- and HF-absorption for municipal waste incineration off gases. It is in principle the same system LURGI uses since the early sixties for calcination of alumina, coal burning and other chemical reactions.

1. General

LURGI, as an engineering company, is designing and constructing nearly all different types of flue gas cleaning systems which are just available on the world market, for instance wet systems, quasi dry processes, regeneration processes - regenerating SO_2 as sulfuric acid or sulfur - and as one of the newest developments: The LURGI dry CFB process. Operating experiences with the first FGD dry commercial sized demonstration plant at SCHWANDORF plant has already been described (1) (5). It showed that this process meets the stringent emission control laws (2) that have come into force in the Federal Republic of Germany since 1983 and which have to be fulfilled by all power plants producing $100 \text{ MW}_{\text{el}}$ ($300 \text{ MW}_{\text{th}}$) or more since July 1st, 1988.

The power plant of BORKEN, owned by PREUSSEN ELECTRA AG, West Germany, is the first commercial sized dry flue gas cleaning system which has been constructed after the SCHWANDORF plant has demonstrated the capability of the process.

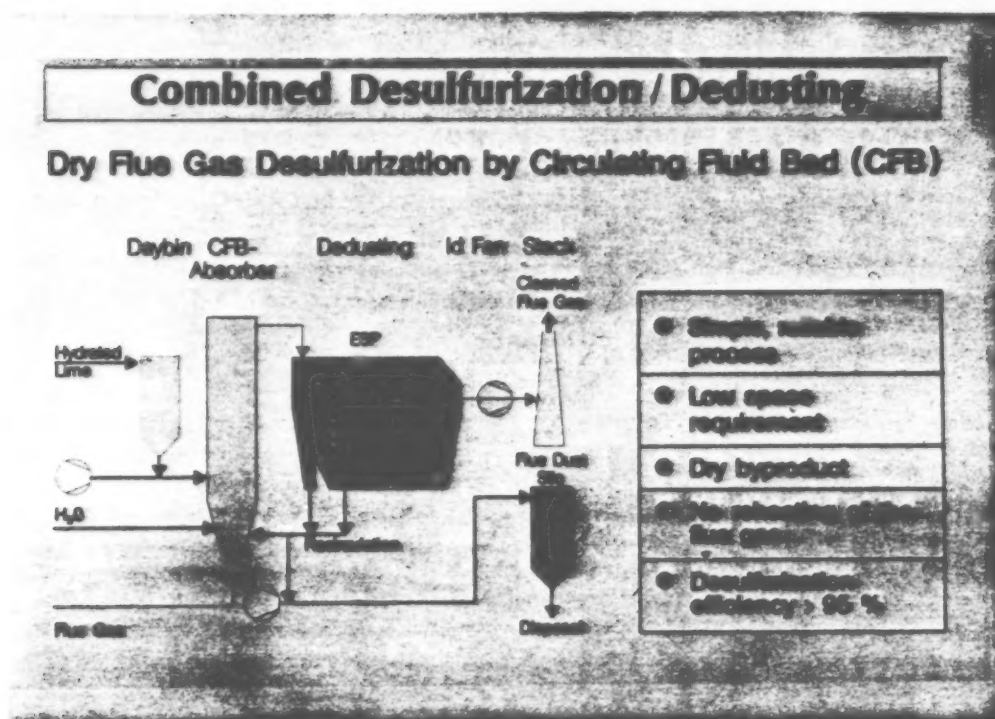
In the following the special operating conditions and experiences of the BORKEN power plant will be reported and some details of the history of the development of this process which is one of the applications of the LURGI expanded circulating fluid bed system (3) (4)

2. The Process

2.1 Process Description

The process has been explained and described in more detail at earlier occasions (1) (5), therefore, only the main characteristics and highlights are pointed out here.

FIGURE 1 shows the simplified flowsheet of the process.



Reproduced from
best available copy.



The raw gas enters the venturi shaped absorber from the bottom through a grid, which consists out of six smaller nozzles, constructed similar to a venturi nozzle. The flue gas dust is partially separated before entering the absorber.

In the circulating fluid bed (CFB) absorber the flue gas will be intensively mixed with the sorbent, which is hydrated lime. SO_2 and SO_3 and other gaseous acid compounds containing in the raw gas react with the hydrated lime forming mainly $\text{CaSO}_3 \times 1/2\text{H}_2\text{O}$, $\text{CaSO}_4 \times 1/2\text{H}_2\text{O}$ and CaCO_3 . The product will be entrained by the clean gas to the top of the absorber and will be separated from the clean gas in the down stream dust collector, which is an electrostatic precipitator or a bag filter.

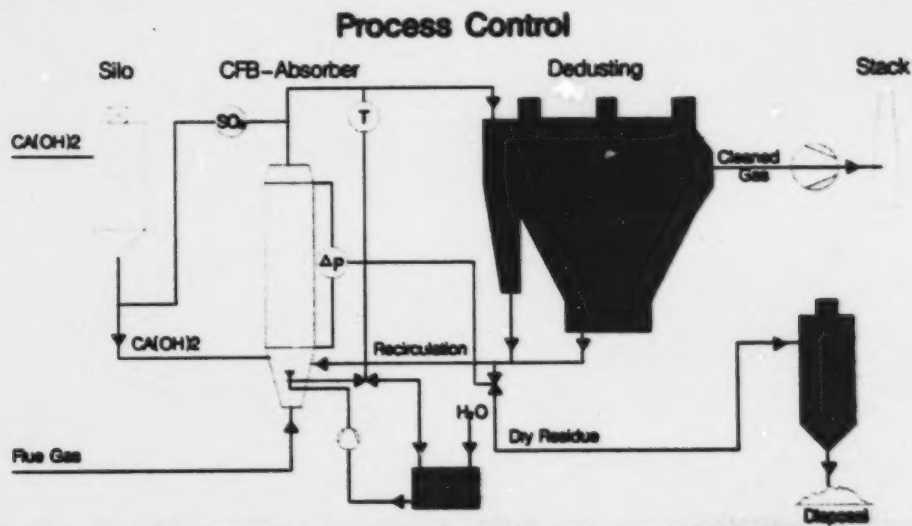
The cleaned gas is sucked by means of an ID fan via a stack to the atmosphere. The separated dust is mainly recirculated back to the absorber via air slides to prolong the solid retention time of the sorbent and to raise the solid loading of the absorber to reduce the Ca/S-mole-ratio of the process. The amount of the product, which corresponds to the hydrated lime fed to the absorber together with the flue dust will be discharged out of the solids circuit and conveyed to the product silo.

Because of the high solids loading of the absorber water can be directly injected into the bottom of the absorber to raise the SO_2 cleaning-efficiency of the absorber, which will be optimized by approaching the absorption temperature to the water dew point. The water injection is independent of the SO_2 content of the raw gas and offers therefore the possibility to operate the absorber close to the water dew point.

2.2 Process Control

FIGURE 2 shows the simplified process control, which effectively consists only of three major control circuits for fully automatic operation, proving that this process is in principle most simple and reliable.

Dry Flue Gas Scrubbing with CFB Absorber



SO₂ Control

The feed of the hydrated lime is controlled by the amount of SO₂ in the flue gas which sets the basic predetermined lime rate for the absorber corrected by the SO₂-clean gas concentration.

At the BORKEN plant the rotation speed of the star feeder for hydrated lime is controlled by this equipment.

Temperature control

The temperature on top of the absorber controls directly the amount of water which will be injected via high pressure return flow nozzles into the bottom of the absorber, that means in more detail, that the return flow valve is directly controlled by the absorber temperature.

Solids Discharge

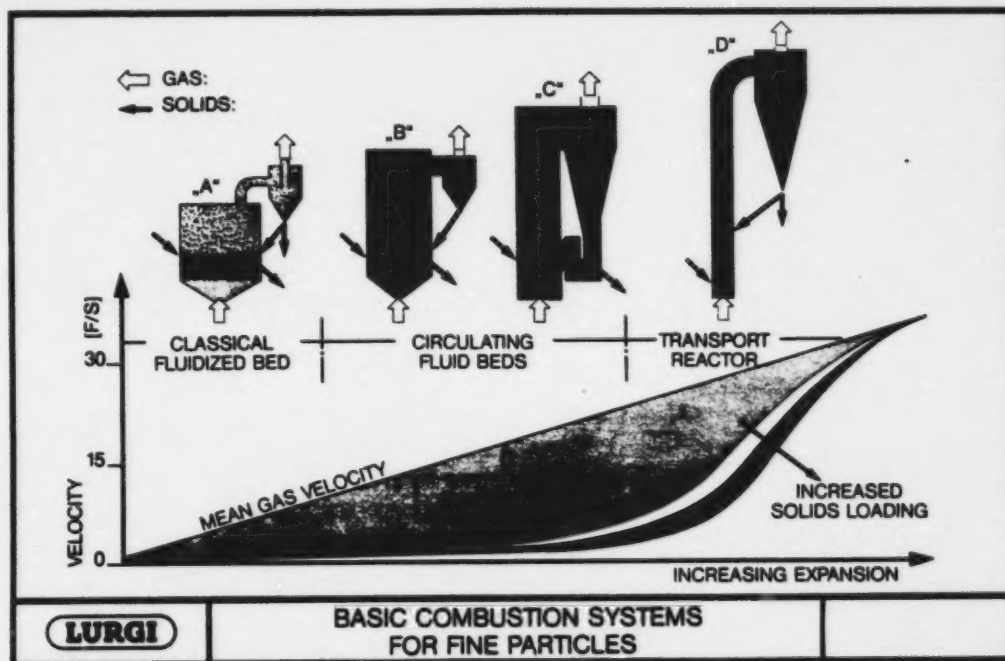
The amount of the dry residue, which will be discharged out of the system is controlled by the solids loading of the absorber. The solids loading of the absorber is measured by the pressure loss along the absorber height which is kept on a constant value. The solid loading or the hold up divided by the solids feed (product and dust) gives the solids retention time of the absorber. It can be changed in wide ranges limited by the suction pressure of the fan and the dedusting efficiency of the precipitator for the maximum value and the flue gas velocity in the bottom nozzles for the minimum value.

BORKEN has got a slightly different solids discharge system: The pressure loss of the absorber is controlled by regulating the recirculated solids about of the ESP by means of a rotary slide valve and the discharged product is controlled by the solids-level of the EPS.bin.

2.3 Process Characteristics

1. Excellent heat and mass transfer behavior

FIGURE 3 gives some explanations for the optimal heat and mass transfer behavior of an expanded circulating fluid bed system.



As it was shown ahead the absorber is operating not only as a chemical reactor for absorbing gaseous contaminations but also as an evaporator, whereas the solids do not change their surface humidity, so that scaling problems can be absolutely avoided.

The excellent heat and mass transfer is achieved by the maximum slip velocity between the solid particles and the fluidizing gas.

For classical or bubbling forming fluidized beds the slip velocity corresponds to the main gas velocity, with which the bed is fluidized. It is relatively small.

Comparably small is the slip velocity also for transport reactors, where the gas velocity is so high, that the particles are entrained as an nearly independent individual single particle, where the slip velocity corresponds to the suspension velocity of the particles in the transporting gas.

In the expanded circulating fluid bed the slip velocity between the average solids velocity and the fluidizing gas has got a maximum. For fluidizing gas velocities which are in between the velocities for a classical fluid bed and a transport reactor and at a sufficient solid loading of the fluidizing gas the particles are forming chains and get a different aerodynamic resistance which allows the solid chains to move contrary to the flowing direction of the fluidizing gas until the slip velocity is so high that the chains will be destroyed and the single particles will again be entrained by the fluidizing air. That explains the typical pulsation of an expanded circulating fluid bed where the particles are always moving up and down inside of the reactor, which is totally filled with a gas-solid suspension.

Further process characteristics are

High mass transfer rate within the lime particles
because of the use of very fine hydrated lime particles,
which have got an average particle diameter of 5
to 10 μm .

Extremely long solids retention time
which allows that peaks of gaseous pollutants can be
absorbed without an additional lime consumption.

Continuous abrasion for the lime particle surface
preventing inactive CaSO_4 -surfaces which cover active
lime particle cores.

Operating temperatures with a close approach to the
water dew point can be achieved which gives a high
utilization of the sorbent.

2.4 Process Features

In the following the process features are summerized:
The process characteristics explain why a

SO₂ removal efficiency of more than 95 % can be achieved.

The BORKEN figures will show that even with flue gases from high sulfur coals even higher SO₂ removal efficiencies have been attained without additional reactions in a bag filter.

The fluid bed absorber is able to reduce any SO₂-content in the raw gas obtained from any coal sulfur content according to any regulations.

The simplicity and reliability with high availability has already been pointed out.

The compactness of the system and large unit capacities we can show at BORKEN as an example.

Typical for the CFB is the simple handling because of

dry reagent feeding, dry residue and no waste water.

Waste water can be used for

water injection, which improves desulfurization and dust collection by an ESP. The water injection is independent and separate from the reagent feed required for desulfurization.

The turndown ration is between 100% and 30% of the boiler load.

3. Reference List and Historical Development of the Process

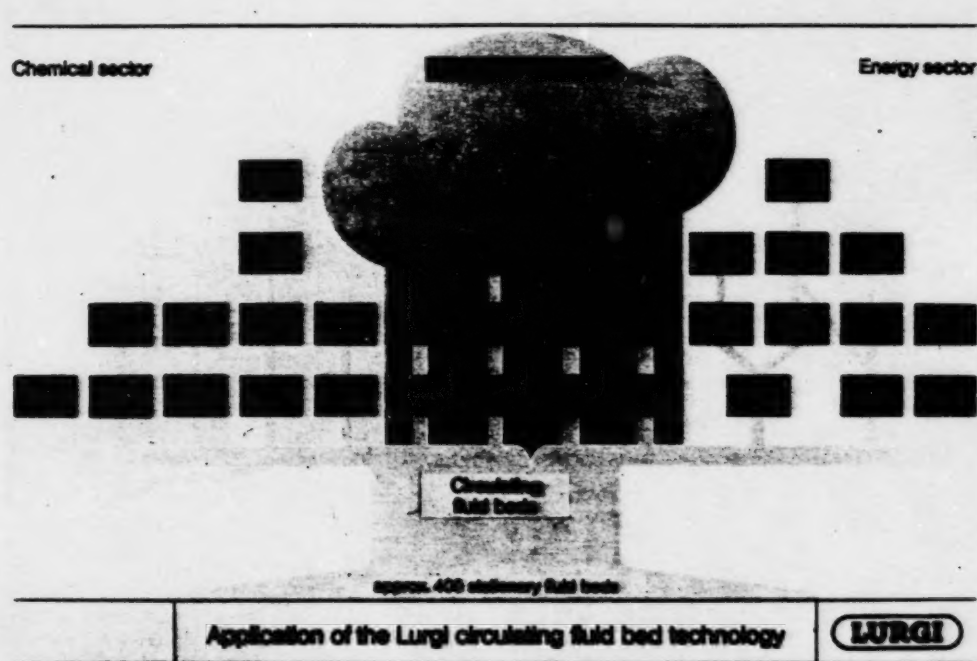
FIGURE 4 gives the list of References of the main plants.

LOCATION OF CUSTOMER	FLUE GAS FLOW RATE (scfm) (ccfm)	REMOVAL % SO ₂ , HCl, HF	DE-DUSTING TYPE SOLIDS (grains/ft ³)	YEAR ORDERED	START-UP
TOEGING VAV BONN	2 x 190.000 2 x 260.000	HF = 99	ELECTRO-STATIC PRECIPITATOR 0.013	1978 DECEMBER	1980 JUNE
NORF VAV BONN	8 x 190.000 8 x 260.000	HF = 99	ELECTRO-STATIC PRECIPITATOR 0.013	1980 DECEMBER	1982 APRIL
SCHWANDORF VAV BONN	3 x 61.300 3 x 120.000	HCl = 95 SO ₂ = 60	ELECTRO-STATIC PRECIPITATOR 0.030	1980 DECEMBER	1982 SEPTEMBER
SCHWANDORF BAG-MUNICH	1 x 155.000 1 x 250.000	SO ₂ = 95	ELECTRO-STATIC PRECIPITATOR 0.060	1983 DECEMBER	1984 NOVEMBER
CONFLANS FOI-FRANCE	1 x 3.900 1 x 4.200	HCl = 90	FIBROUS FILTER 0.013	1984 JUNE	1984 DECEMBER
BORKEN PREAG-HANNOVER	1 x 392.000 1 x 630.000	SO ₂ = 97	ELECTRO-STATIC PRECIPITATOR 0.035	1985 MARCH	1987
SIERSDORF EBV-MERZOGENRATH	2 x 240.000 2 x 355.000	SO ₂ = 93	ELECTRO-STATIC PRECIPITATOR 0.021	1986 MARCH	1988
UNTERVAZ/SWITZERLAND BCU	1 x 165.000 1 x 265.000	SO ₂ = 90	ELECTRO-STATIC PRECIPITATOR 0.021	1986 JULY	1988
 LIST OF REFERENCES FOR: DRY/SEMI-DRY FLUE GAS SCRUBBERS USING A CIRCULATING FLUID BED ABSORBER					

It shows that the first commercial sized system using an expanded circulating fluid bed reactor was used and developed for adsorbing gaseous HF out of waste gases from an aluminum reduction plant (6). The HF-removal efficiency is 99 %, the clean gas concentration less than 1 mg/Nm³. This process development started in the early 1970's. The first industrial application of the circulating fluid bed principle, developed by F. Schytil (4) and L. Reh(3), started in the 1960's and was used for calcining of alumina.

In the late 1970's the gas cleaning process has been modified for the dechlorination of off gases of waste incineration plants, and in the early 1980's this process was used for desulfurization of flue gases of coal fired power stations.

FIGURE 5 shows what has happened in between.



Today LURGI offers 31 different applications using the expanded circulating fluid bed system.

4. The Flue Gas Desulfurization Plant at the BORKEN Power Plant of PREUSSEN ELECTRA AG, West Germany

4.1 Power Plant Data

The power plant which flue gases has to be cleaned has got a generating capacity of approx. 100 MW_{el} (Unit III) and is a dry bottom boiler which went on stream 1964. Unit II has got a capacity of 64 MW_{el}, a wet bottom boiler only used, as a standby, which went on stream 1961.

4.2 Design Data

The following data give the coal analysis, which is typical for the high-sulfur lignite from the area surrounding BORKEN:

Coal Analysis:

Moisture content	43 - 50 %
Ash content	6 - 20 %
Heating value	11.090 KJ/kg (4770 BTU/lb)
Sulfur	4 - 8 % Waf

The following table lists the inlet flue gas data:

Flow rate 225.000 - 620.000 m³/h (135.000 - 370.000 scfm)
(The minimum value is 36 % of the maximum value.)

Temperature	120°C - 165°C (250° - 330°F)
Dust content	16-25 g/m ³ (7-11 grains/ft ³)
SO ₂	9 -13 g/m ³ (3100 - 4500 ppm)
CO ₂	7,5 - 10,5 Vol. %
O ₂	6 - 8,5 Vol %
H ₂ O	15 - 18 Vol %

Clean gas data:

Absorption temperature 68°-70°C (154°-158°F)

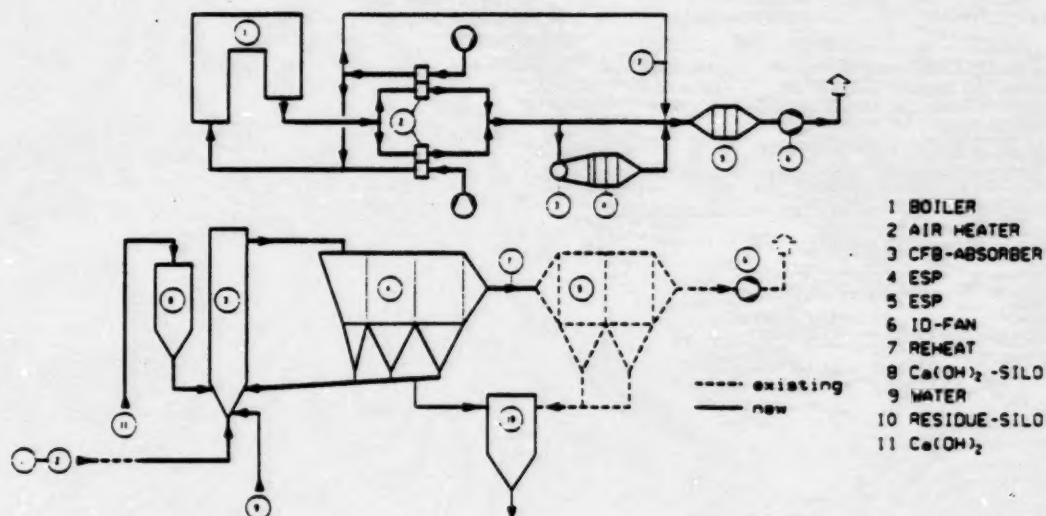
(Stack temperature 75°-80°C (170°-180°F)

Dust content less than 80 mg/m3 (0,035 grains/ft)

SO₂ less than 400 mg/m3 (140 ppm)

4.3 Layout of the system

FIGURE 6 shows a simplified diagram of Unit III,

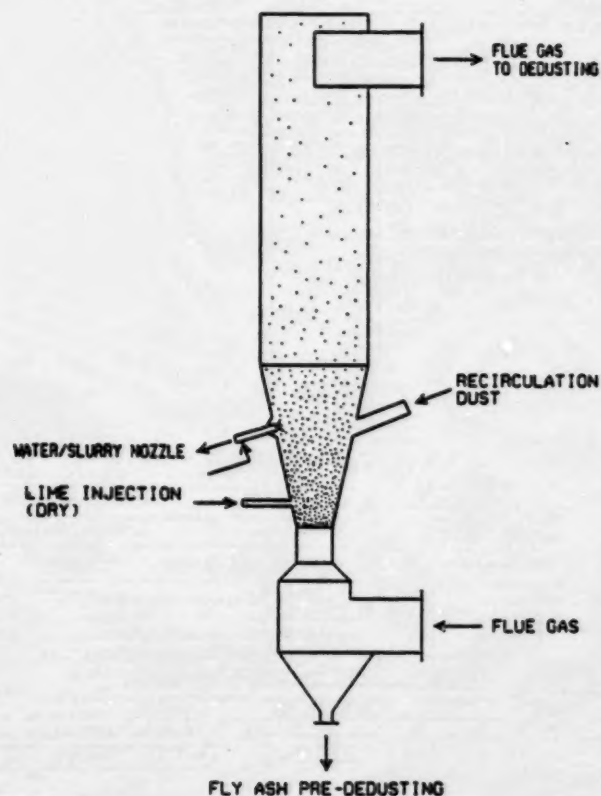


Number 3 and 4 indicating the CFB Absorber with the new ESP, downstream, number 5, the old ESP.

The plant consists of:

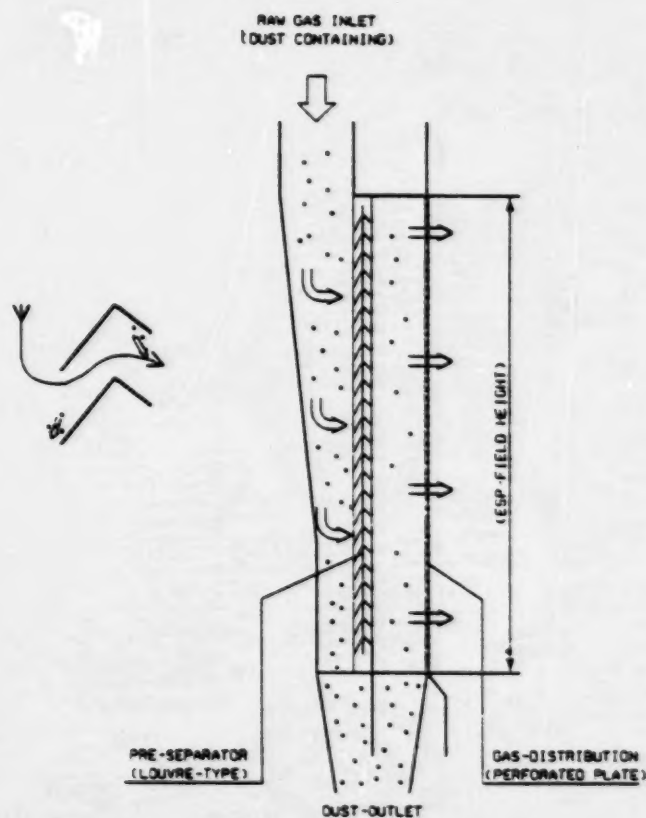
- the raw gas duct
- the fluid bed absorber
- the two field electrostatic precipitator
- the existing precipitator, two fields
- the water injection system
- dry hydrated lime feed system
- dust conveying equipment for recirculating and discharge
- bins for hydrated lime and residue

FIGURES 7 shows the simplified fluid bed absorber with the fly ash prededusting the feed points for hydrated lime, recirculated dust and injected water.



The flue gas inlet is a 6 venturi nozzle grid.
The absorber is absolutely empty with an inner diameter of 8,5 m and has no special internals which can be eroded. The material is carbon steel.

FIGURE 8 shows the prededusting and gas distribution upstream of the new ESP.



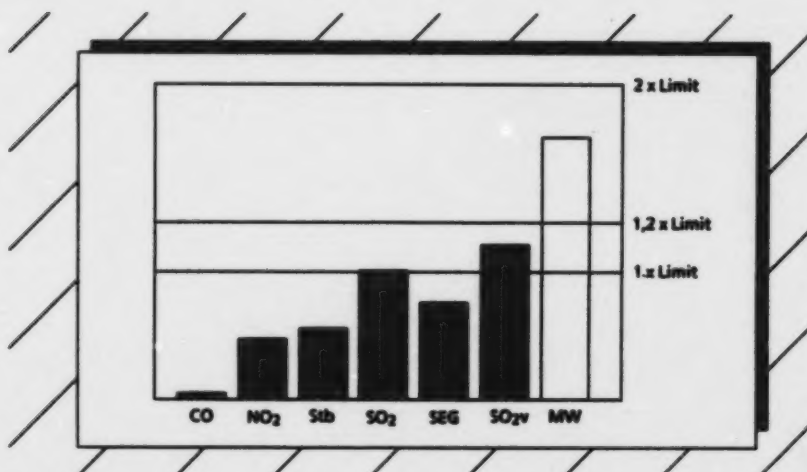
4.4 Operating Experiences

4.4.1 Desulfurization Efficiency

The following FIGURES 9 and 10 are showing operating datas from the BORKEN plant, as copies of the emission rate calculator prints.

Power Plant Borken, Boiler III Operating Data

LURGI



The most important value is the sulfur emission rate, which can be calculated as an 1 minute average value (FIGURE 9) and as a 24 h development, representing half hours average values.

Power Plant Borken, Boiler III Sulphur Emission Rate

LURGI

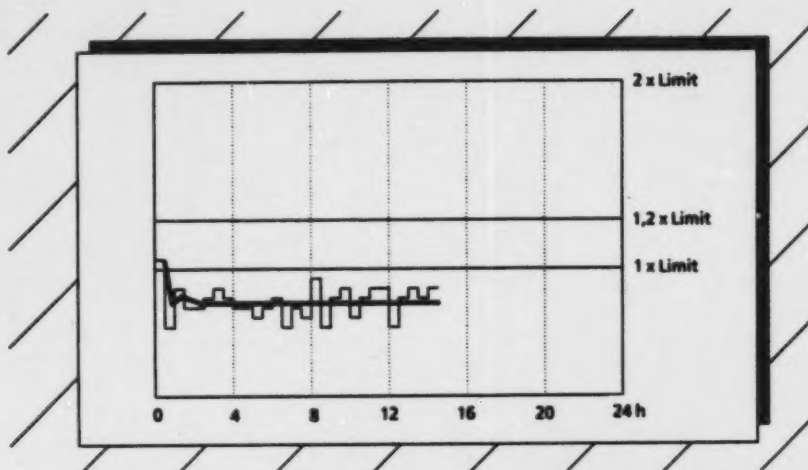


FIGURE 10 shows that the sulfur emission rate or the desulfurization efficiency since the start up of the plant end of 1987 has never been a problem, though the BORKEN power plant summerizes some extreme operating conditions for a flue gas desulfurization system, for instance

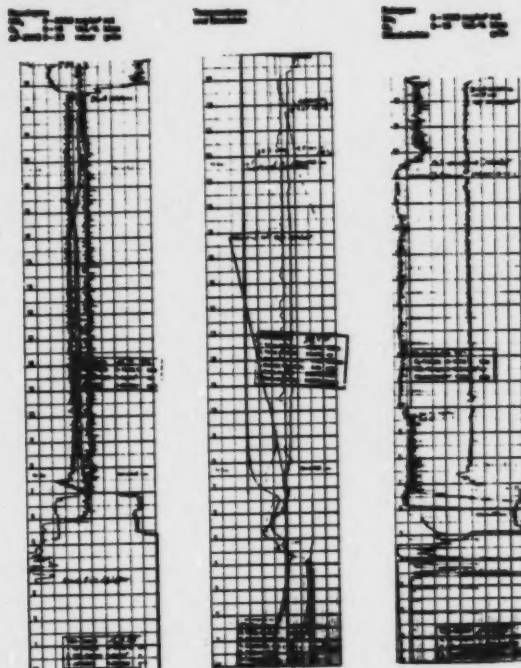
- extreme high SO_2 and dust contents in the flue gas
- a wide range of the flow rate changing from 36% to 100% of the designed value
- cleaning of different types of flue gases, one of a dry bottom boiler with low combustion temperature and high SO_3 and dust concentrations (Unit III) and one of a wet bottom boiler with high combustion temperatures and low SO_3 and dust but even higher SO_2 values, both with a high water dew point of approx. 55°C , which will be raised by water injection up to approx. 61°C .

4.4.2

Start up and shut down of the plant

Technische Abgrenzung
in der abschließenden Widerholung

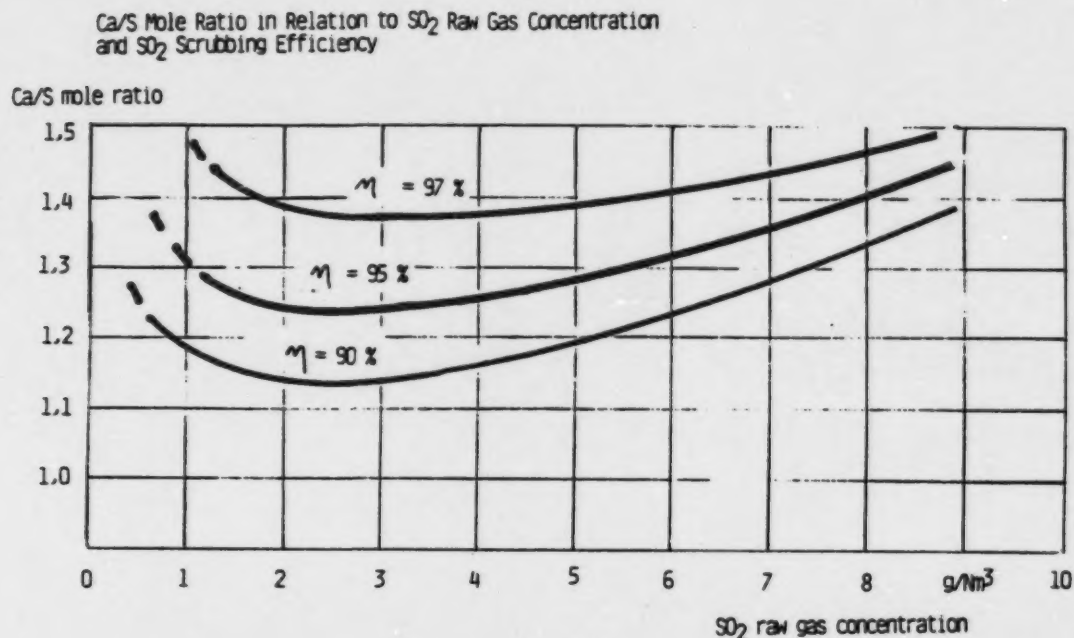
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FIGURES 11 shows how quickly the system can be started and the desulfurization immediately occurs with the built up of the circulating fluid bed and the water injection.

4.4.3 Ca/S mole ratio

FIGURE 12 shows the Ca/S mole ratio in relation to the SO₂ scrubbing efficiencies.



The experiences of BORKEN have proven, that very high SO₂ raw gas concentrations influence the Ca/S mole ratio because of reducing the solid retention time in the absorber of the active sorbent hydrated lime. The same influence has the dust content of the flue raw gas. At BORKEN the dust content of up to 30 g/m³_n reduces the retention time of the hydrated lime in the absorber for approx. 50 %.

At very low clean gas SO₂-concentrations (less than 50 mg/m³_n) a raising of the lime consumption has been obvious.

This diagram is only valid for one gas velocity.

The next picture shows, that the mole ratio is influenced by the gas velocity, too.

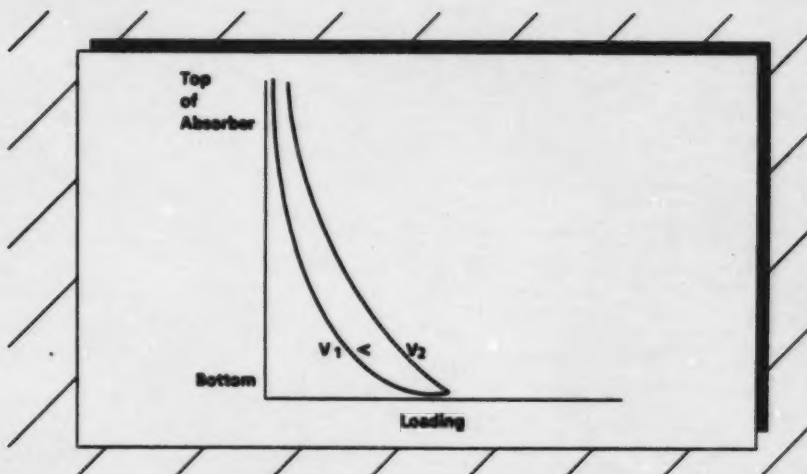
4.4.4

Partial Load Operation

FIGURE 13 explains the solid loading of the absorber at different gas velocities and the solid distribution along the height of the absorber.

Solid Loading at different Gas Velocities

LURGI



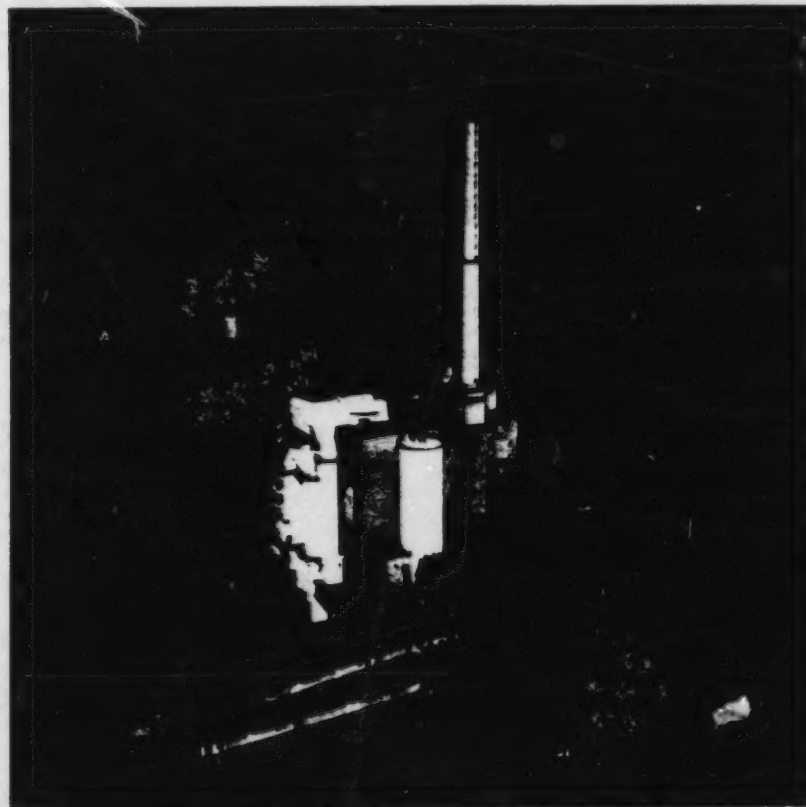
At a certain gas velocity the solid loading of the absorber decreases from the bottom to the top of the reactor. With decreasing gas velocities the solids distribution changes by partially settling of the solid hold up down to the bottom of the absorber. The desulfurization efficiency on the top of the absorber will be reduced, the lime consumption or the Ca/S-mole ratio raises.

Because of the reduced gas velocity in the venturi nozzles, the pressure loss will be reduced too. At very low flue gas flow rates the solids loading of the absorber has to be reduced because the flue gas can no more lift the solids loading or part of the bed leaves the absorber down through the nozzles.

For partial gas loading conditions lower than 30 % of the designed value a recirculating of the cleaned gas will be provided.

This for instance will be done for our newest order we recently have got from OPEL GMBH, Rüsselsheim, which belongs to U.S. General Motors.

The following picture shows a photo of the BORKEN plant.



5. Summary and Conclusions

This paper presents the dry circulating fluid bed process for flue gas desulfurization developed by LURGI. This process is one of the more than 30 different applications of the expanded circulating fluid bed system, LURGI has developed in the past 25 years.

The positive operating experiences of the flue gas desulfurization plant of the BORKEN power plant of PREUSSEN ELECTRA, West Germany, has been reported.

The operation conditions of this plants include some extreme values like high SO_2 and dust concentration in the flue gas, a wide changing of the flow rate and a high water dew point, typical for high sulfur lignite coal from the surrounding BORKEN area.

The special characteristics and features of this dry process have been pointed out.

BORKEN is one more positive example for the LURGI circulating fluid bed system, with which LURGI is able to supply a proven second-generation dry desulfurization process which is technically and economically superior to many other dry processes currently available.

- - - -

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Scale-Up Testing of the ADVACATE Damp Solids Injection Process

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ABSTRACT

Recent advances toward the scale-up and commercialization of the ADVACATE Damp Solids Injection Process include sorbent preparation by pressure hydration and development of the damp injection process as a stand-alone flue gas desulfurization/flue gas cleaning technology for both fossil fuel and waste-fired application.

Pressure hydration enables the production of calcium silicates from flyash and lime via both dry and slurry modes, as well as significantly reducing the time of sorbent preparation from over 10 h to 1-2 h. The majority of research has been conducted in the slurry mode, where the degree of calcium utilization has been found to be directly related to the surface moisture content of sorbent at injection. Up to 26-percent-moisture silicates have been successfully injected with a screw feeder, with the corresponding calcium utilizations exceeding 50 percent on a once-through basis. The implications are that utilizations similar to those for spray dryers may be obtained with high moisture silicates and sorbent recycle via in-duct sorbent injection.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The Advanced Silicate (ADVACATE) Process is an in-duct dry injection flue gas desulfurization (FGD) process which uses highly reactive calcium silicate hydrates as the sorbent. As illustrated in Figure 1, the sorbent can be produced by mixing a calcium-containing material, such as lime, and a silica-containing material, such as flyash or recycled solids, in water at an elevated temperature and pressure. The calcium silicate hydrates produced have high surface area, usually greater than 20 m²/g. The surface structure of the calcium silicate hydrates produced also allows them to flow freely as dry materials at a moisture content up to 35 percent by weight. The damp, free-flowing hydrates can be handled by conventional dry powder transporting and injection apparatus. The large surface area and the high moisture retention capability of the calcium silicate hydrates make them very reactive toward sulfur dioxide (SO₂) and far better sorbents than hydrated lime for a dry injection FGD process.

Under EPA sponsorship, Jozewicz and Rochelle started to investigate the flyash recycle effects in spray drying FGD in early 1982 (Jozewicz and Rochelle, 1986). They found that reactive calcium silicate hydrates can be produced by slurring flyash with lime at temperatures below 100 °C (atmospheric hydration), but relatively high flyash/lime ratios (greater than 3) and long reaction time (over 10 h) are required. However, test data suggested that the hydrates were not suitable for use in the spray drying FGD processes due to operating problems such as wet deposition and scaling (Jozewicz et al., 1988a). Later developments showed that calcium silicate hydrates are very reactive sorbents for SO₂ removal when injected dry into a humidified flue gas stream (Jozewicz et al., 1987). Further research was conducted in an effort to reduce the flyash/lime ratio and reaction time required for sorbent preparation. Bench-scale test results showed that reactive calcium silicate hydrates were produced when the flyash/lime slurry was mixed at temperatures above 100 °C (pressure hydration). The reaction time was reduced to less than 4 h and the flyash/lime ratio to less than 3 (Jozewicz et al., 1988b).

Flyash/lime ratio and reaction time are two important factors for commercial application of the ADVACATE process. A high flyash/lime ratio would increase flue gas dust loading and could overload an existing particulate control device. The long reaction time would increase the hydrator/mixer size and capital cost. Thus, a relatively short residence time is needed to develop a continuous and economic sorbent preparation process.

The bench-scale data revealed the potential of pressure hydration to lower the flyash/lime ratio and shorten the reaction time. It was decided to scale-up the pressure hydration operation from bench-scale to pilot-scale to investigate further the production and application of calcium silicate hydrates as dry injection FGD sorbents. This paper summarizes the scale-up test results on pressure hydration and characterizes the behavior of damp calcium silicate hydrates in an FGD application.

TEST FACILITY

A detailed description of the bench-scale test facility has been presented by Jozewicz (1988a and b). This section will discuss the pilot-scale facility used for scale-up tests and compare it with the bench-scale facility.

SORBENT PREPARATION

The pilot-scale pressure hydrator (Figure 2) was a unit specially designed for achieving efficient mixing of solids and liquids at elevated temperatures and pressures (up to 1825 kPa or 250 psig). This unit is manufactured by Littleford Brothers, Inc., and designated as Model DVT-130. The DVT-130 unit features a horizontally mounted, cylindrical vessel with a total volume of 0.122 m³ (4.6 ft³) in which the material is mechanically fluidized by plows mounted on a central shaft. The shaft rotates along the inner surface of the vessel. Plows are also provided for achieving optimum mixing of the solids with the liquid phase, if applicable. Normally, a batch of around 45.5 kg (100 lb) solids (lime plus flyash) and 54.5 kg (120 lb) water was loaded through the lid in the stack, the unit was closed and sealed, and the agitation was started. The chemical reaction occurring was monitored by the thermocouple and the manometer provided with the unit. Normally, a

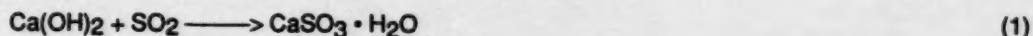
temperature of 148.9 °C (300 °F), or 446 kPa (50 psig) was aimed at. The product could also be heated by the use of steam to the jacket surrounding the vessel, with steam normally supplied at 446 kPa (50 psig) or about 148.9 °C (300 °F). The sorbent preparation was normally 1-2 h or less duration. The unit was then depressurized by gradually opening the ball valve (mounted on the side of the stack) and by allowing the excess vapor to escape. After the pressure had been released as indicated by the manometer reading, the product was normally cooled by flowing cooling water through the jacket and continuing the mixing for 10-20 min. The prepared product was next discharged from the hydrator, and depending on the product's water content, it was either filtered by a rotary drum vacuum filter followed by filter cake drying in an oven, or the filtration step was omitted and the product was transferred directly to an oven for drying. The dried cake was crushed and ground to a fine powder for use as the sorbent for the pilot-plant dry injection tests.

Compared with the bench-scale pressure hydrator used by Jozewicz (1988a and b), the pilot-scale unit provides considerably better mixing and temperature control. Table 1 compares the features of the bench- and pilot-scale pressure hydrators.

DRY INJECTION PILOT PLANT

The reactivity of the calcium silicate hydrates produced in the pressure hydrator was evaluated in a dry duct-injection FGD pilot-plant. The pilot-plant facility, shown in Figure 3, consists of a gas humidifier equipped with a rotary atomizer for atomization of water to control the gas temperature and humidity. Air flow is drawn from ambient air through an air filter and an electrical heater. The heated air enters the humidifier through an air disperser located in the center of the chamber roof. After the humidifier, the gas flows through a heat-traced and insulated duct section and a pulse-jet baghouse for collection of solids. Gaseous SO₂ was injected into the heated air before the humidifier to simulate the flue gas from burning sulfur containing fuel. Calcium silicate hydrates were injected by a screw feeder into the duct downstream of the humidifier. The 5-cm (2-in.) diameter, 24.5-m (80-ft) long duct contains the humidified gas stream with entrained solids as it flows to the pulse-jet baghouse. The flue gas duct residence time is estimated to be almost 2 s. The collected solids are discharged batchwise from the baghouse hopper. A detailed description of the pilot plant is provided by Jorgensen et al., 1987.

The sorbent reactivity is represented by lime utilization—the percentage of lime injected that is reacted with absorbed SO₂—according to the following chemical reaction:



The lime utilization was obtained from pilot-plant data by dividing the amount of SO₂ absorbed by the amount of lime used to prepare the sorbent that was injected.

Compared with the bench-scale test facility (Jozewicz et al., 1988a and b), which is a fixed-bed reactor running on a batch basis, the pilot-test facility provided a more realistic SO₂ absorption device to simulate the dry injection process on a continuous flow basis. Table 2 shows a comparison of the bench-scale reactor with the dry-injection pilot plant.

RESULTS AND DISCUSSION

PRESSURE HYDRATOR

As illustrated by Figure 4, there are two modes of operation when using the pressure hydrator for calcium silicate hydrate sorbent preparation. The wet-mode operation produces a slurry from the pressure hydrator. Further sorbent processing such as drying, grinding, or mixing is required for the final preparation of the sorbent for dry injection uses. With proper control of the water/solids ratio and the liquid/solids loading sequence, dry-mode operation can produce a dry powder as the product, which can be directly used as dry injection sorbent without further processing.

The pilot pressure hydrator was first operated using wet-mode sorbent preparation procedure W-A (Figure 4). This procedure was based on the bench-scale pressure hydrator recipe. A slurry containing 67 percent water was obtained after pressure hydration. The slurry had to be filtered before drying to reduce the drying time and energy requirement. Pilot-plant test results (Test No. 1 of Table 3) show that a 33-percent lime

utilization was obtained when sorbent prepared according to procedure W-A was used for dry sorbent injection SO₂ removal at a 11.1 °C (20 °F) approach. Pilot pressure hydrator test No. 2 employed procedure W-B to reduce the water/solids ratio and resulted in a slurry containing 54 percent water, which is similar to the filter cake water content of Test No. 1. It was decided to dry the 54-percent solids slurry and omit filtering. The pilot-plant test showed that the sorbent prepared according to procedure W-B (Test No. 2 of Table 3) was at least as reactive as that from procedure W-A. Since procedure W-B is simpler and more efficient than procedure W-A, procedure W-B was adopted as the normal operating procedure for the pilot pressure hydrator operation.

Extensive pressure hydration tests were conducted to evaluate the effect of hydration time on the reactivity of sorbent. Figure 5 shows a comparison of the reactivity of sorbents prepared with pressure hydration, atmospheric hydration, and without hydration. It shows that only 10- to 12-percent lime utilization was obtained when only Ca(OH)₂ (without hydration with flyash) was the sorbent. With atmospheric hydration, more than a 12-h hydration time was required to raise the sorbent reactivity to 30 to 40 percent lime utilization. However, when pressure hydration was used to produce the sorbent, only 1 to 2 h hydration time was needed to make the sorbent achieve 30 to 40 percent lime utilization. Figure 5 also shows that no beneficial effect of atmospheric hydration was obtained at such (1 to 2 h) short hydration time. It was concluded that the pilot pressure hydrator was effective for producing high reactivity calcium silicate hydrate sorbent and that its use could reduce the hydration time to less than 2 h.

Another set of tests was performed with the pilot pressure hydrator to evaluate the effect of flyash/lime ratio on sorbent reactivity. Test No. 3 of Table 3 shows that at a 3:1 flyash/lime ratio, the lime utilization was 45 percent when the damp sorbent (containing 25 percent moisture) was used in the dry injection pilot plant. Test No. 4 decreased the flyash/lime ratio to 2:1, and the resulting sorbent moisture content was 15 percent. The dry injection results for this test showed that the lime utilization reached 52 percent. Although more data are needed to confirm the high reactivity of the sorbent used in Test No. 4, the results indicated the potential of reducing the flyash/lime ratio by more than 33 percent with pressure hydration.

A series of tests was conducted to operate the pilot pressure hydrator on dry-mode (procedure D-A, Figure 4). The objective was to control the amount of hydration water so that a moist but free-flowing product was produced. Several problems were encountered during this test series. First, poor product recovery rate limited the throughput to less than 50 percent. The majority of the reagent accumulated as deposits and scales on the wall and the plows of the pressure hydrator. Second, the hard, thick deposits hampered the operation and maintenance of the pressure hydrator. Third, the flyash/lime mix seemed to have gone through a "mud" stage before the "dry-mode" operation was completed. The "mud" stage required excessive power for mixing and tripped off the power unit. Due to the simple concept of "dry-mode" operation and the potential economic benefit, more tests are planned to further evaluate the operability/reliability of the "dry mode" pilot pressure hydrator operation. Studies of several different types of nozzles to control the hydrator water addition rate and spray pattern are planned. Alternate water/flyash/lime loading sequences to avoid the "mud stage" will also be studied.

DAMP SORBENT INJECTION RESULTS

Depending on the degree of drying, the calcium silicate hydrates produced contained up to 26 percent free moisture and still maintained the free flowing characteristics. These damp powders when squeezed by hand would form small but loose agglomerates. However, the agglomerates would readily become powders when a slight mechanical shear such as that from a solids screw feeder was applied. No plugging, blocking, or scaling problems with this sorbent were experienced during the pilot-plant dry injection tests. No accumulation of the injected sorbent inside the ductwork, as reflected by pressure drop, was encountered. The pulse-jet baghouse was running at a pressure drop of up to 10 cm (4 in.) of water without any cleaning difficulties.

It was found that the extent of humidification could be reduced when damp sorbent was injected for SO₂ removal. This is reflected by the temperature profile measured across the pilot plant as shown in Figure 6. When bone dry sorbent (moisture content less than 5 percent) was used, the humidifier outlet temperature had to be approximately the target approach to saturation temperature (e.g., 11.1 °C or 20 °F), to maintain the desired temperature level at the baghouse outlet. There was a slight temperature drop of about 0.55 °C (1 °F) through the duct to the baghouse inlet due to heat loss. However, a 1.1 to 1.7 °C (2 to 3 °F) temperature increase was obtained across the baghouse when bone dry calcium silicate hydrates were used as the sorbent. As opposed to

the temperature decrease which would normally be measured when conventional sorbent such as lime is used, this temperature increase is believed to be due to the reaction between calcium silicate hydrates, moisture, and SO_2 .

On the other hand, when damp sorbent (such as sorbent containing 25 percent moisture) was injected, the humidifier outlet temperature did not have to be as low as in the bone dry case. Figure 6 shows that with damp sorbent, instead of a 11.1°C (20°F), a 25°C (45°F) approach to saturation was maintained at the outlet of humidifier. The gas phase temperature decreased significantly through the duct and only slightly across the baghouse. It should be noted that there was only about 2 s of gas residence time between the humidifier outlet and the baghouse inlet. It is apparent that most of the temperature drop and flue gas humidification was accomplished in that short a time. Figure 6 indicates that the load and size of the humidifier can be significantly reduced when damp calcium silicate hydrates are used as the dry injection sorbent. Furthermore, the humidifier may be eliminated if sufficient moisture is injected with the damp sorbent and all the flue gas humidification is accomplished by sorbent-carried moisture in the duct as shown by the dashed curve in Figure 6. More tests are planned to demonstrate the "dry injection without humidifier" concept by using the recycle mixing sorbent preparation procedure (W-C, Figure 4) to supply the quantity of damp sorbent needed. For practical application, an efficient economizer is desirable to decrease the flue gas temperature and to improve the energy recovery.

After each pilot-plant test, solid samples were taken from the baghouse for free moisture analysis. Figure 7 shows the comparison of solids' moisture content before and after the dry injection tests. It shows that, regardless of how dry or damp the sorbent was initially, most baghouse product moisture content falls between 5 and 7 percent. Since all the pilot dry injection tests were conducted at about 11.1°C (20°F) approach to saturation at the baghouse outlet, Figure 7 suggests there may be a gas-solid moisture equilibrium between the humidified flue gas and the calcium silicate hydrates. Figure 7 also suggests that, when sorbent containing less than 5 to 7 percent moisture was injected, the water vapor from the flue gas actually condensed as free moisture on the surface of sorbent particles. It is likely that the condensed vapor formed water films around the sorbent particles and reacted with calcium silicate and SO_2 , as reflected by the temperature increase across the baghouse shown in Figure 6. On the other hand, when damp sorbent was injected, Figure 7 indicates that the sorbent actually lost free moisture and experienced a drying process, which confirms the data presented in Figure 6. Figure 6 also shows that the free moisture lost was evaporated to humidify the flue gas and lower the gas phase temperature in the duct.

Figure 8 shows the sorbent reactivity measured as a function of sorbent moisture. It indicates a trend of increasing lime utilization with increasing sorbent moisture. Thus, the higher sorbent moisture would be expected to result in a more reactive sorbent. It should be noted that, although the data in Figure 8 were obtained with the baghouse outlet temperature controlled at about 11.1°C (20°F) approach to saturation, the actual temperature profile experienced by various sorbents, as illustrated in Figure 6, differs. Also, the gas phase mass transfer involved is also different for damp sorbent and bone dry sorbent. As illustrated in Figure 9a from a global point of view, SO_2 and water vapor were diffusing countercurrently from the bulk gas to the gas/solid interface when damp sorbent was injected into the flue gas. On the other hand, SO_2 and water vapor diffuse concurrently when bone dry sorbent is used (Figure 9b). Another factor which may have a major impact on SO_2 absorption rate is the quantity of sorbent surface moisture that is available during the dry injection process. Klingspor et al. (1984) suggested that SO_2 absorption is a function of the number of water monolayers on the sorbent surface. It was proposed that, when the number of surface water monolayers is large enough, the H_2O molecule would interact with SO_2 and form a $\text{SO}_2 \cdot n\text{H}_2\text{O}$ complex, which would then react with the sorbent. The SO_2 absorption rate was determined by the complex formation rate which can be enhanced by increasing the surface moisture content. It is apparent that the damp calcium silicate hydrates contain a sufficient amount of surface moisture throughout the dry injection process, whereas the bone dry sorbent probably does not have sufficient surface water monolayers until some flue gas water vapor is condensed. It is clear from Figure 8 that damp calcium silicate hydrates were more reactive than the dry hydrates when used as sorbents in the pilot-scale dry injection SO_2 absorption tests.

SUMMARY AND CONCLUSION

1. Highly reactive ADVACATE sorbent for dry injection SO₂ removal can be produced by pressure hydrating lime and flyash at 148.9 °C (300 °F) and about 446 kPa (50 psig).
2. Compared with atmospheric hydration, pressure hydration can reduce the ADVACATE sorbent preparation time from over 10 h to 1-2 h. The flyash to lime ratio can also be substantially reduced.
3. Damp ADVACATE sorbent containing 26 percent free moisture was successfully tested in the pilot plant. High lime utilization (over 50 percent) was obtained and no solids handling problems were encountered.
4. A positive relationship between ADVACATE sorbent reactivity and free moisture content was observed during the pilot-plant test. The data suggest that the sorbent reactivity increases with increasing free moisture content.
5. The moisture content of the pilot plant baghouse products falls in the range of 5 to 7 percent regardless of the initial sorbent moisture level. The narrow range of baghouse product moisture indicates that there is probably an equilibrium relationship between solid phase moisture content and gas phase humidity which determines the product moisture level.

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Table 1. Comparison of Bench-Scale and Pilot-Scale Pressure Hydrators

Parameters	Bench scale	Pilot scale
Operation mode	Batch	Batch
Size, L	0.3	130
Production rate, kg/batch	0.05	50
Temperature control		
Heating	Electrical	Steam
Cooling	None	Cooling water

Table 2. Comparison of Bench-Scale and Pilot-Scale Dry Injection Test Facilities

Parameters	Bench scale	Pilot scale
SO ₂ absorption device	Fixed bed	Dry injection (duct followed by baghouse)
Operation mode	Batch	Flow
Sorbent use, kg/h	0.001	0.5~4
Flue gas flow rate, L/min	4.7	140
Average sorbent residence time, min	60	20~40

Table 3. Pressure Hydration Test Results

Test No.	1	2	3	4
<u>Pressure hydrator</u>				
Temperature, °C (°F)	148.9 (300)	148.9(300)	148.9 (300)	148.9 (300)
Mode	Wet	Wet	Wet	Wet
Procedure	W-A	W-B	W-B	W-B
Flyash/lime ratio	3/1	3/1	3/1	2/1
Slurrying time, h	1	1	1	1
Slurry water, %	67	54	54	53
Filtration	Yes	No	No	No
Sorbent moisture, % (after drying)	3.7	3.5	25	15
<u>Dry Injection Test</u>				
Temperature, °C (°F)				
Humidifier, in	176.7 (350)	176.7 (350)	176.7 (350)	176.7 (350)
Humidifier, out	51.7 (125)	51.7 (125)	65.6 (150)	60.0 (140)
Wet bulb	40.6 (105)	40.6 (105)	40.0 (104)	40.0 (104)
Baghouse, in	51.1 (124)	51.1 (124)	51.7 (125)	51.7 (125)
Baghouse, out	52.8 (127)	53.3 (128)	51.1 (124)	51.1 (124)
SO ₂ concentration, ppm	1,500	1,500	1,500	1,500
SO ₂ removal, %	60	61	81	94
Stoichiometric ratio	1.8	1.8	1.8	1.8
Lime utilization, %	33	34	45	52

1. Wet-mode operation

(W-A) pressure hydration ———> filtration ———> drying ———> grinding ———> dry injection

(W-B) pressure hydration ———> drying ———> grinding ———> dry injection

(W-C) pressure hydration ———> recycle mixing ———> dry injection

2. Dry-mode operation

(D-A) pressure hydration ———> dry injection

Figure 4. Pressure hydrator operation modes

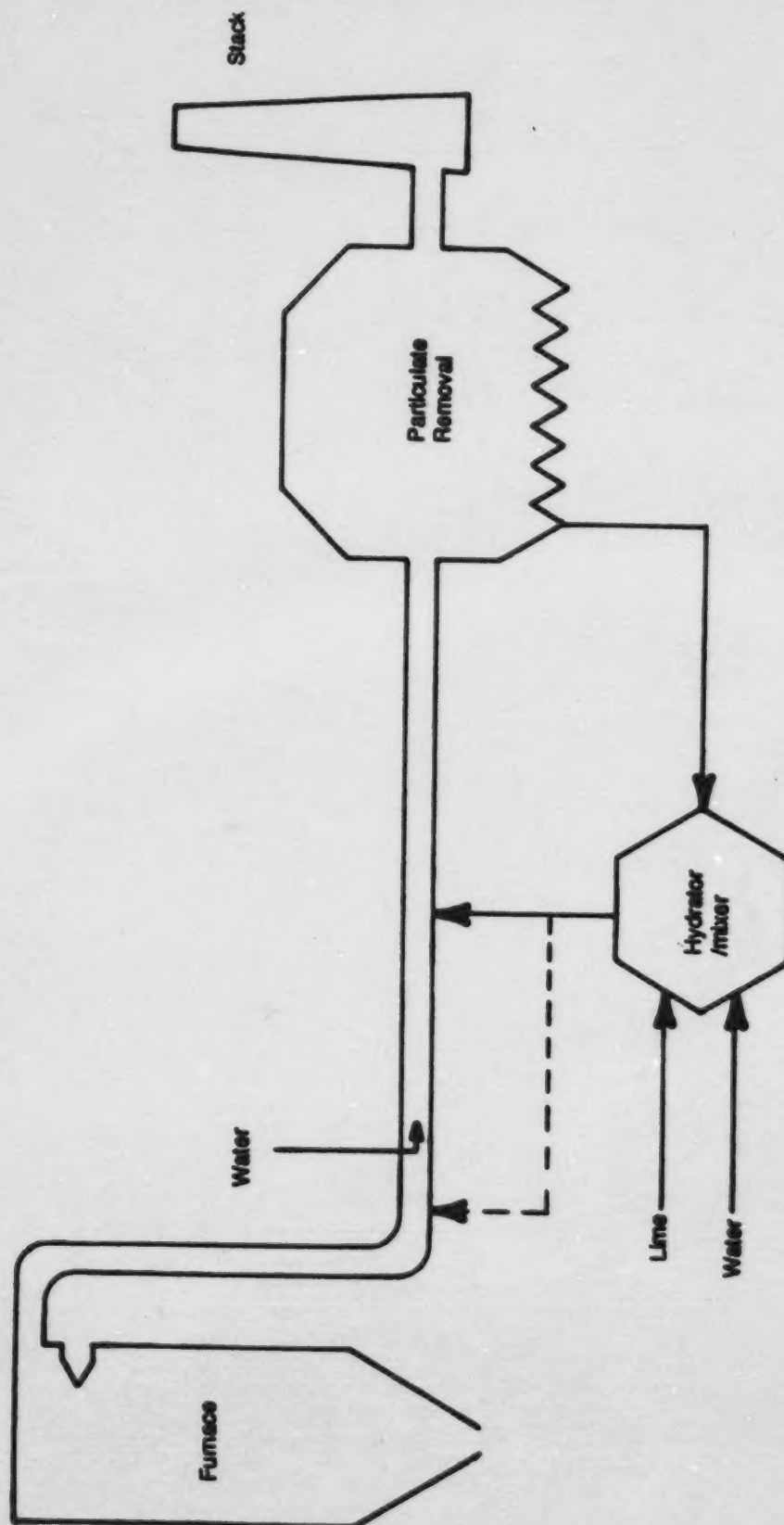


Figure 1. Schematic of Advacate FGD process concept.

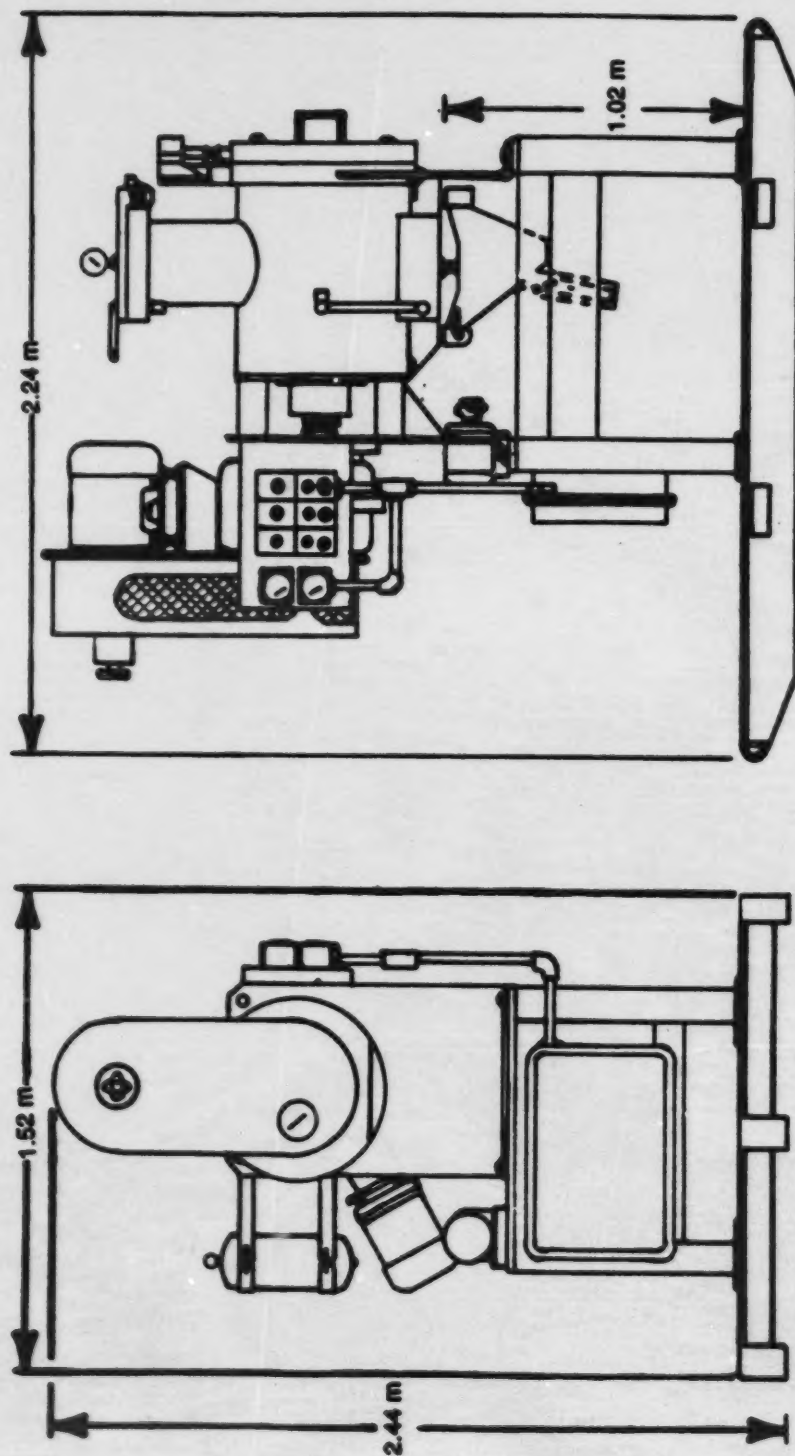


Figure 2. Schematic of pilot-scale pressure hydrator.

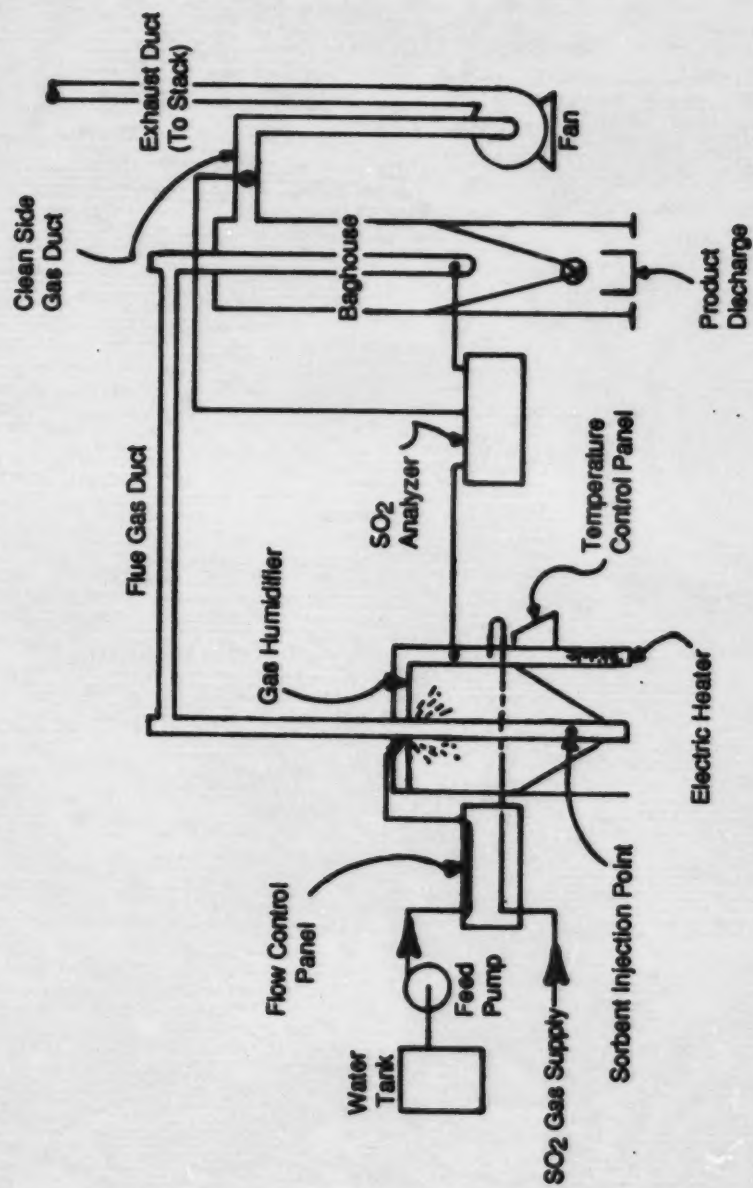


Figure 3. Schematic of duct-injection pilot facility.

1. Wet-mode operation

(W-A) pressure hydration ———> filtration ———> drying ———> grinding ———> dry injection

(W-B) pressure hydration ———> drying ———> grinding ———> dry injection

(W-C) pressure hydration ———> recycle mixing ———> dry injection

2. Dry-mode operation

(D-A) pressure hydration ———> dry injection

Figure 4. Pressure hydrator operation modes

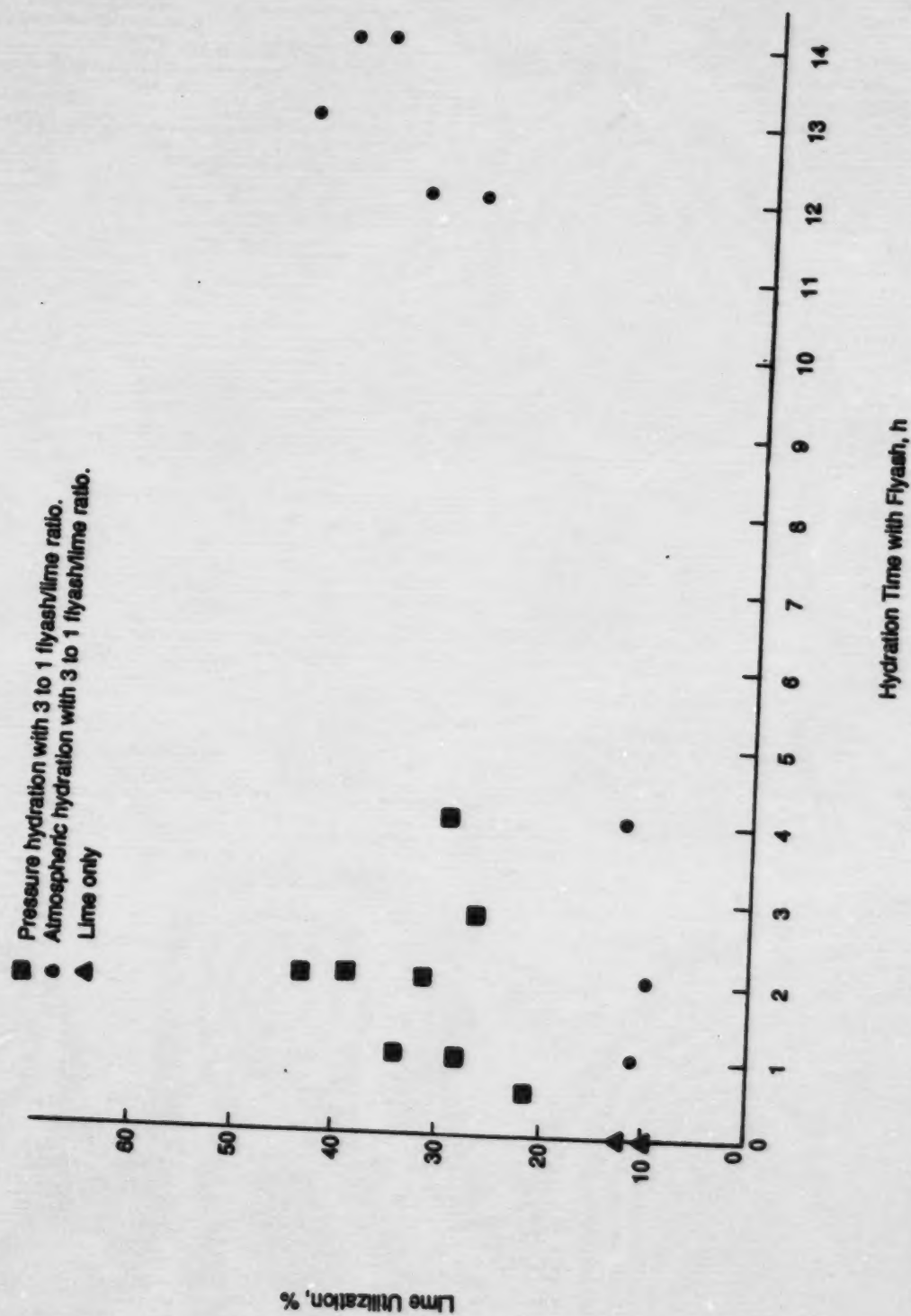


Figure 5. Effect of hydration time on sorbent reactivity at 11.1 °C (20 °F) approach to saturation.

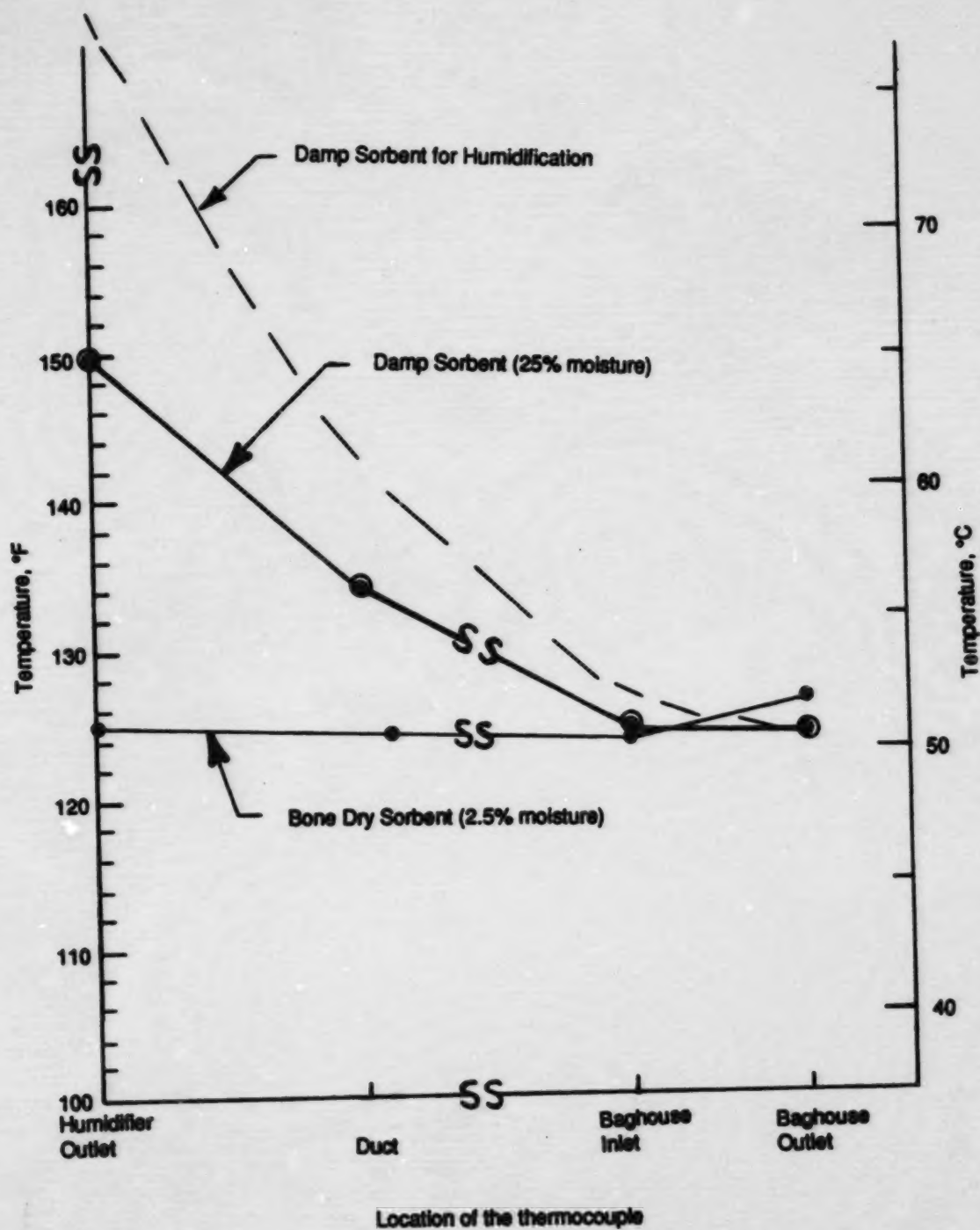


Figure 6. Temperature profiles across the dry injection pilot plant.

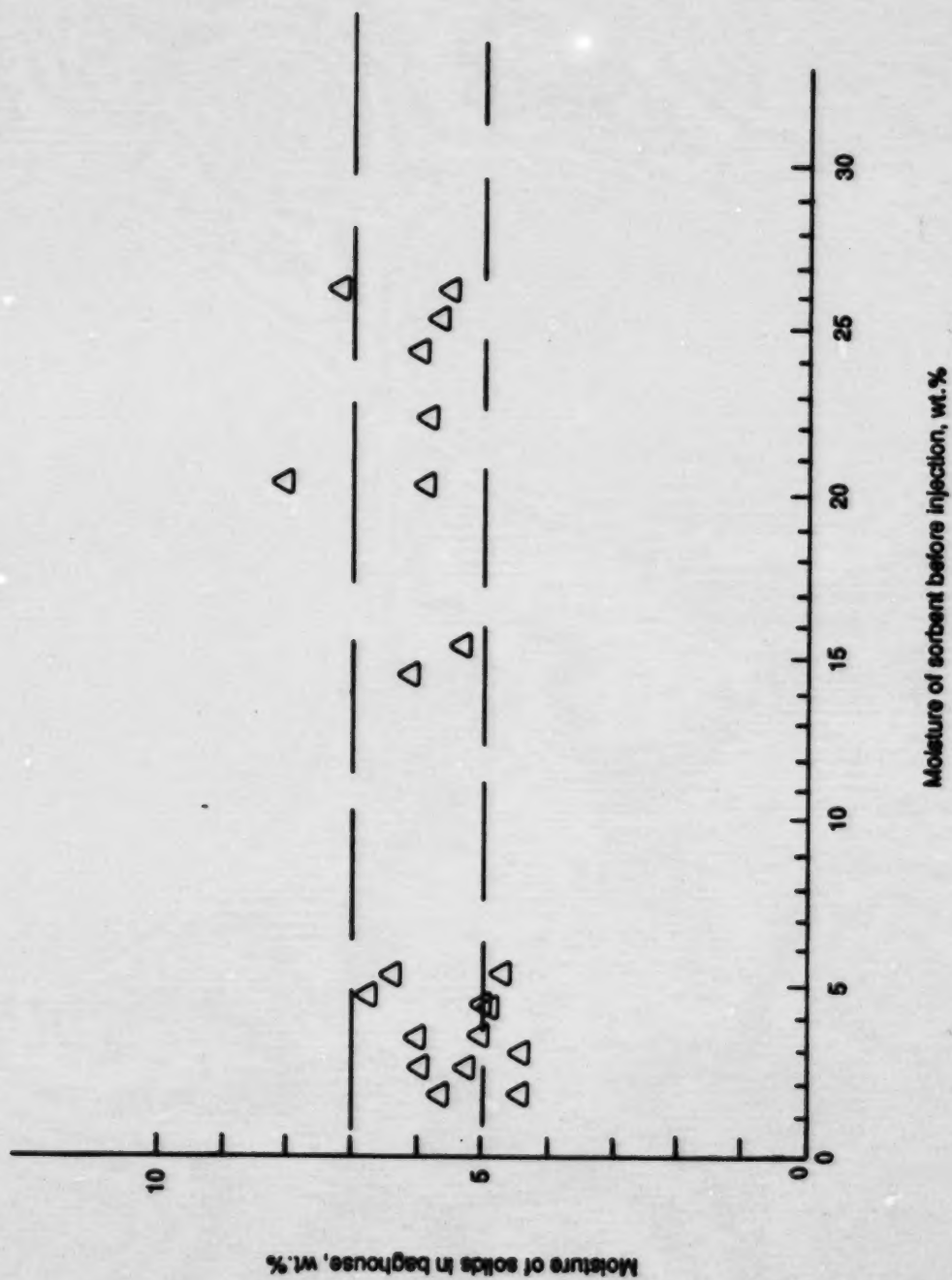


Figure 7. Solids moisture content before and after dry injection.

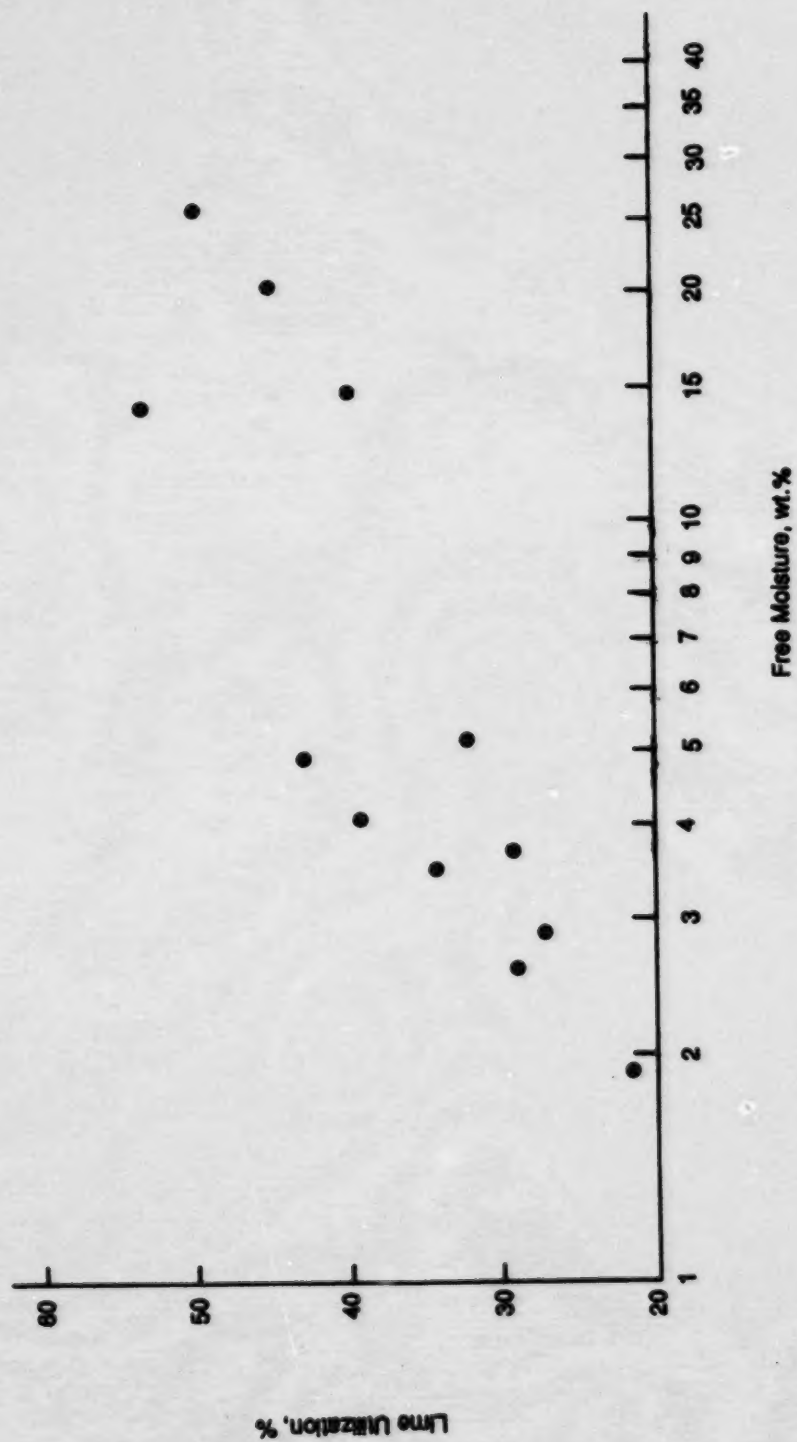


Figure 8. Lime utilization as a function of sorbent moisture content.

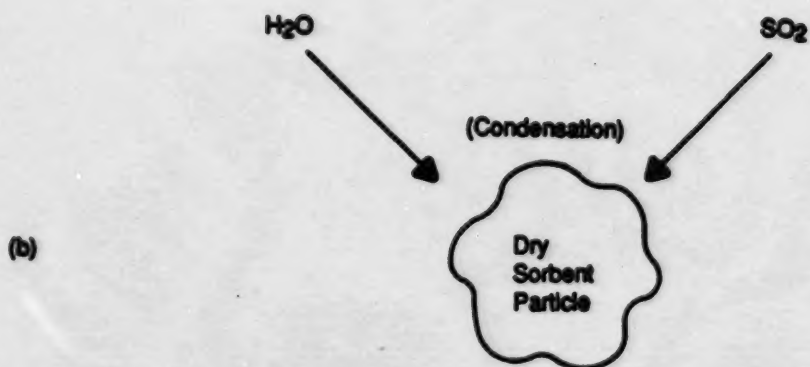
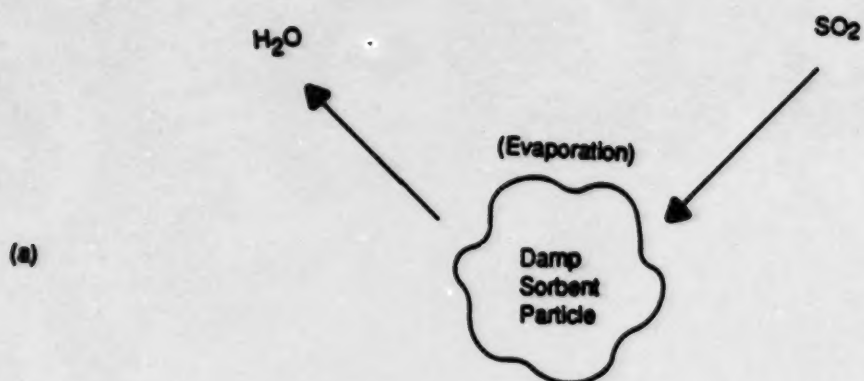


Figure 9. Global gas phase mass transfer involved in damp and dry sorbent SO_2 absorption.

DRY FLUE GAS DESULFURIZATION PROCESS USING ABSORBENT
MADE FROM FLYASH

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ABSTRACT

A dry flue gas desulfurization process has been developed. In this new process, fly ash (coal ash) which usually is discarded at a power station is utilized as a raw material of the SO₂ absorbent.

From basic study it was proved that the chemical reactions of this new absorbent with SO₂ are very different from those which occur during desulfurization employing for the typical lime injection or semi-dry absorption methods.

A demonstration plant test with flue gas capacity of 50,000m³N/h was conducted at the Ebetsu Power Station of The Hokkaido Electric Power Co., Inc., for about one year and will be finished in this year. 90% SO₂ removal was attained under the condition of 1.05-1.10 Ca/S molar ratio.

Feasibility study of commercial plant will be soon initiated.

The test results made it clear that this plant could be operated without problems such as increase in pressure drop due to accumulation of dust.

INTRODUCTION

In recent years, acid rain has become one of the most significant causes of environmental problems throughout the world, particularly in Europe and Northeast America. Therefore, industrialized nations should be very much concerned with reducing emissions of pollutants from such stationary sources as boilers and furnaces.

Air pollution brought about serious health hazards in Japan back in the mid-1960s, resulting in the enactment of very severe emission standards. Almost all fossil fuel fired power plants in Japan are now equipped with desulfurization facilities. The wet-type limestone-gypsum method is widely being adopted with high performance and reliability as the basic method of controlling SO₂ emission from power plants. As for the wet process, however, there are some drawbacks such as much consumption of utility water and the necessity for waste water treatment. In this respect, dry systems may eventually become a better solution.

Coal-fired power plants emit, in addition to such environmental pollutants as SO_x and NO_x, a tremendous amount of coal ash, which corresponding to as much as 10-30% of the original coal. Therefore, it is very important in respect to the generation cost of electricity and environmental protection to establish a technology for dealing with the coal ash economically and steadily.

To comply with the situation described above, we introduce here a new dry FGD process which uses a solid absorbent made from coal ash and lime. The research and development work of this process, the basic principle of which was clarified by The Hokkaido Electric Power Co., Inc., has been carried out since 1985 jointly by The Hokkaido Electric Power., Hitachi, Ltd., and Babcock-Hitachi K.K. The present paper is concerned with the principle and the outline of the test results for its commercialization.

CONCEPT OF THE PROCESS

FEATURES OF THE PROCESS

The main features of the present process are listed in Table 1, which compares this with the dry injection methods. The most noteworthy feature of this new process is that SO₂ removal of over 90% can be attained at such a low Ca/S molar ratio as 1.05-1.10. This should be contrasted with the Ca/S ratio of 3-5 which is required for dry lime injection process to achieve a similar removal efficiency. The present high calcium utilization degree allows the spent absorbent to be discarded without the problem of elevating the pH of ambient water.

The present absorbent, which is obtained by using coal ash as a raw material, is very economical to produce, and is also easy to handle because it is non-inflammable, in contrast with carbaceous absorbents.

OUTLINE OF THE PROCESS

A schematic description of principle of this FGD process is shown in Figure 1.

Absorbent

The raw materials of the present absorbent are coal ash, lime and gypsum. The spent absorbent from the absorber is reused as a supply source for gypsum at a stationary state of operation. The raw materials are mixed first together with water to give a paste having a viscosity suitable for extrusion. After being shaped into small pieces by extrusion, the material is subjected to steam-curing at nearly 100°C for 6-15 hours, and then dried almost completely at 130°C.

The pellets undergo hydration during steam-curing to increase the hardness, while the combined water is expelled on drying, resulting in the formation of micropores suitable for the penetration of SO₂ from the flue gas.

Absorption of SO₂

Absorption of SO₂ is carried out in a moving-bed type absorber packed with absorbent pellets. The fresh absorbent pellets are supplied from the top of the absorber, and move down through the absorber. The pellets, while moving through the absorber, are exposed to flue gas that is to be treated and react with SO₂ in it to form CaSO₄.

Spent Absorbent

A favorable characteristic of this process is that the spent absorbent is basically a mixture of CaSO₄ (calcium sulfate anhydride) and coal ash, in contrast with CaSO₃ in the case of other processes. The spent absorbent can be discarded without increasing COD (chemical oxygen demand) and pH of the ambient water, a part of this being reused for the production of fresh absorbent as shown in Figure 1.

FUNDAMENTALS OF PRODUCTION AND PROPERTIES OF THE ABSORBENT

PRODUCTION OF THE ABSORBENT

The present absorbent was found as a derivative result of the studies which were carried out to obtain materials of high strength from coal ash. Certain results of studies on the relation between the production condition and the desulfurization activity of the solid materials are shown in Table 2, indicating clearly that steam-curing followed by thermal treatment is essential to high activity, and that the usage of coal ash is effective to enhance the activity.

Many studies were carried out to develop the production methods which are suitable for mass production. From the results, the following aspects were clarified : (a) the mixture of raw materials, which consists of slaked lime, gypsum, coal ash and water, is impossible to be directly shaped into small pellets due to its fluidability similar to raw concrete. From the slurry of this state, however, the solid absorbent pellets are obtained by solidifying to some extent by steam-curing for about 2 hours at nearly 100°C, crushing, pelletizing, additional steam-curing and then drying at 130°C, (b) the spent absorbent, which is a state of absorbent after SO₂ absorption and is obtained from the bottom of the absorber, is very useful as a source of CaSO₄, because this material accelerates the hydration of the slurry, allowing the direct extrusion of raw mixture without preliminary steam-curing, in contrast with the case when CaSO₄·2H₂O is used.

The production method described in (b) has been used in a demonstration plant, showing that the absorbent pellets of the desired properties were obtained by this method. The standard flowsheet of the production method is shown in Figure 2, and the effect of the kinds of coal ash on the activity are shown in Table 3. The optimum conditions for composition of raw materials and steam-curing are slightly different from coal ash to coal ash. It has been clarified, however, that all coal ash ever tested can be used as a raw material. The role of coal ash in the formation of solid material is considered to be a supply source of Al₂O₃ and/or SiO₂, the detail of which is now being studied.

SO₂ ABSORPTION PROPERTIES

The effect of the composition of gas to be treated on the velocity of SO₂ absorption is shown in Table 4. It is clear that the maximum velocity of SO₂ absorption is observed in the concomitant presence of NO, O₂ and H₂O, and that, therefore, the velocity decreases drastically even only one of these components is omitted. Of these gaseous components, the concentration of NO_x in the flue gas depends on the type of the combustion facilities and conditions, therefore the design and operation conditions of the desulfurization plant should be decided, taking the concentration of NO_x in the flue gas into consideration.

SO₂ is absorbed and oxidized simultaneously to form CaSO₄. This phenomenon shows that, in the production of the absorbent, the only material to be supplied from outside the power station is lime, which assures that the present FGD process is very economical.

KINETIC STUDY OF DESULFURIZATION REACTION

Concept of Reaction of SO₂ with Absorbent

The absorbent which is utilized in this desulfurization process has a large number of pores, hence the SO₂ in the flue gas can easily penetrate the absorbent particles.

The reaction can be supposed to proceed as follows : SO₂ in the gas surrounding the absorbent initially reacts on the surface of the pellet. A layer of product CaSO₄ is formed, which grows forward the center of the pellet. Subsequently reactions occur only after SO₂ diffuses through this product layer and contacts the unreacted absorbent surface.

Reaction Kinetics of SO₂ Absorption

In the model employed, the rate of absorption of SO₂ by the absorbent gradually decreases with time. A typical example of the relationship between weight gain, due to reaction with SO₂, of the absorbent and reaction time is shown in Figure 3.

This type of behavior can be described by following formula ;

$$\frac{dQ}{dt} = K_1(Q_s - Q) + K_2 Q_s \quad \dots\dots (1)$$

where Q is weight gain of the absorbent due to SO₂ absorption, Q_s is the value corresponding to the saturated state, and K₁ and K₂ are rate coefficients which are determined from Figure 3. Q is found to be related to properties, such as gas temperature and concentrations of SO₂, NO, and O₂. All of these effects on the reaction rate have been measured, so this formula is applicable to wide variety of gas conditions.

Basic Design of Absorber

When flue gas quantity to be treated is given, the dimensions of moving-bed absorber can be determined by the equation (1) and the mass balance of sulfur in the absorber expressed by following equation.

$$u \frac{\partial c}{\partial x} + v \frac{dQ}{dy} = 0 \quad \dots\dots (2)$$

where u and v are gas velocity and absorbent moving velocity in the moving-bed absorber, respectively. c is SO₂ concentration in flue gas.

In this paper, the results of demonstration plant test are compared with the expected values which are calculated from equations (1) and (2).

TESTS FOR COMMERCIALIZATION

PILOT SCALE TEST

Following the above mentioned laboratory studies, a pilot-scale test was conducted in 1985-1986 to collect data necessary to make this process practicable.

The absorber used in this pilot test was moving bed of rectangular cross section, 2400mm high by 600mm wide by 1400mm deep. Absorbent pellets are pulled down through the absorber by gravity, before being discharged from an exit port at the bottom. Coal-fired boiler flue gas flows horizontally through the packed absorber bed.

SO₂ Removal Efficiency

Figure 4 shows the relation between SO₂ removal efficiency (η_{SO_2}) and the Ca/S ratio, where Ca is the number of moles of Ca (added as lime to the supply absorbent) entering the bed per unit time, and S is the flow rate, in moles/time, of SO₂ in flue gas. It can be seen that η_{SO_2} increases with increasing Ca/S, and values of η_{SO_2} in excess of 90% can be obtained for Ca/S ratios greater than 1.2~1.3.

Calcium Utilization

Figure 5 shows the calcium utilization efficiency (η_{Ca}) of the absorbent in the absorber exposed to the flue gas for a long period of time. It is observed that η_{Ca} of absorbent decreases moving toward the gas exit ; hence, the average of η_{Ca} of the discharge will not be high.

Gas Pressure Drop

It was noted that the gas pressure drop in the absorber increased with decreasing absorbent moving velocity (V_z). When V_z fell below limiting value of V_z the pressure drop increased abruptly. This behavior is believed to be caused by

dust (fly ash) contained in the flue gas at concentrations ranging from 60mg/m³N to 300mg/m³N. Sampling of the absorbent pellets in the bed revealed that almost all the dust was trapped by a layer of pellets lying within 300mm from the gas inlet to the reactor.

Comparison between Measured η_{SO_2} and Calculated Value

Figure 6 shows a comparison between the measured η_{SO_2} and calculated values. This comparison was performed to confirm the accuracy of the set of equations described previously. In both cases, the predictions and measurements were in good agreements, suggesting that the present numerical model may be applied to the design of reactors.

From this result described above, following points have been revealed ;

- (1) A dust removal tower with high moving velocity of absorbent is required for reducing gas pressure drop.
- (2) A second absorber should be added upstream of the main absorber to improve η_{ca} of the discharge (absorbent is discharged from the main absorber and fed into the second absorber). On the basis of this consideration, it is proposed that a double tower-type absorber should be employed in the next stage of this study.

DEMONSTRATION TEST

Following the pilot-scale test, a demonstration plant test was carried out. The principal design specifications are as follows :

Gas flow rate	50,000m ³ N/h
Inlet SO ₂ concentration	550ppm
SO ₂ removal efficiency	90% or more
Calcium utilization efficiency	80% or more
Boiler fuel	Coal
Gas temperature	140°C
Moisture content in flue gas	9vol%

A view of the demonstration plant is shown in Figure 7.

Absorber Design

The main points which shall be considered when designing an absorber are that absorbents are forced to reside for a long time in the absorber as the moving velocity is relatively low and consequently the pressure drop through the absorber increases by accumulation of the dust contained in the flue gas. Three types of absorber were studied by changing the absorbent moving patterns. The results are shown in Table 5. As a result of the case study on the absorber design, it was noted that type-3 (double tower type) absorber was suitable for attaining high absorbent utilization without increasing the gas pressure drop. The space velocity SV (gas flow rate/volume of packed absorbent) of 400h⁻¹ was required to attain 90% SO₂ removal efficiency when adopting this type of absorber. It is also expected that calcium utilization of 97% can be attained at this condition.

System Description

The flow sheet of this demonstration plant is shown in Figure 8. The system consists of an absorbent production process and SO₂ absorption process.

Absorbent Production Process

Coal ash, lime and spent absorbent, which are raw materials for the production of absorbent, are stored in each silo, are fed out by the feeder, kneaded with water and then shaped into small pieces by an extruder. The extruded pellets, which are steam-cured to obtain desulfurization activity and hardness, are dried virtually completely. The dry pellets, once stored in a silo, are supplied to the absorber

with the amount necessary for SO₂ absorption. A photograph of the produced absorbent pellets is shown in Figure 9.

SO₂ Absorption Process

Most of the dust contained in the flue gas is collected in the pre-absorber and a part of SO₂ is also absorbed and removed in the pre-absorber. In the main absorber, fresh absorbent contacts with the flue gas and nearly all SO₂ is removed. The flue gas is induced by a boostup fan which is installed at the outlet side of the main absorber. After the absorption of SO₂, the absorbents, which are discharged from the bottom of main absorber, are supplied to the top of the pre-absorber. The pellets move down through the pre-absorber at a velocity faster than that of the main absorber so as to remove the dust and to avoid increasing the pressure drop caused by dust accumulation in it, where η_{ca} of absorbent is improved by further SO₂ absorption.

Operation and Control

The plant is operated at a distance using a CRT display from a central control room. The operating status of auxiliary equipment such as start/stop, alarm display, indications are visible and operable on the CRT display in the control room.

Test Results

It is known that space velocity is one of the most important factor when designing absorbers. Therefore, a test has been carried out to confirm the effects of SV on desulfurization characteristics by changing SV. As one of the test results, SO₂ removal efficiency, calcium utilization efficiency and pressure drop at the condition of SV=555h⁻¹ was shown in Figure 10. The inlet SO₂ concentration fluctuated between 280 ~ 450ppm and the average was approximately 390ppm. The η_{SO_2} of 89 ~ 93%, η_{ca} of more than 80% and the pressure drop of 163 ~ 178mmAq were obtained. Based on SV and Ca/S variation tests, it was clarified that an optimum value of SV could be selected with corresponding to the inlet SO₂ concentration.

SV Variation Test

A desulfurization performance can be calculated by solving the SO₂ absorption rate equation and the material balance equation as described before. Table 6 shows the comparison of the predicted and measured value of η_{SO_2} and η_{ca} at SV=370, 550 and 740h⁻¹. The larger the SV is, the smaller η_{SO_2} is, however, η_{ca} hardly changes.

Ca/S Variation Test

Figure 11 shows a correlation between η_{SO_2} and η_{ca} at SV=555h⁻¹ when changing Ca/S ratio. It was clarified that η_{SO_2} was improved but η_{ca} deteriorated with increasing Ca/S. A good correspondence between the calculated (solid line) and measured value was obtained. SO₂ removal of 90% could be obtained under the condition of Ca/S=1.05-1.10.

Dust Removal

The absorber can trap the dust simultaneously such as a granular bed dust collector while absorbing SO₂. Figure 12 shows the characteristics of dust removal at SV=400h⁻¹. In proportion to the inlet dust load increases, the outlet dust increases. The dust cocentration at the absorber outlet was less than 20mg/m³N. It is also observed that the dust load at the absorber outlet increases with increasing the absorbent feed rate. Therefore, the dust load at the absorber inlet shall be determined corresponding to the required dust load at the absorber outlet.

CONCLUSIONS

A study of a newly-developed desulfurization process revealed that high levels of SO₂ removal more than 90% could be attained for Ca/S=1.05-1.10.

The production process for the present absorbent has been determined. It was observed that no significant differences existed in the absorption ability of absorbent produced from different types of coal ash.

In the moving bed absorber employed for the reaction of SO_2 with the absorbent, problems such as an increase in pressure drop due to deposition of dust contained in flue gases did not occur during about ten months long run.

The solid spent absorbent discharged from the absorber pose no environmental hazard because of their high utilization more than 80% and, hence, may be freely discarded or used in landfills.

Pilot and demonstration plant tests have yielded basic data for the design of commercial plants.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

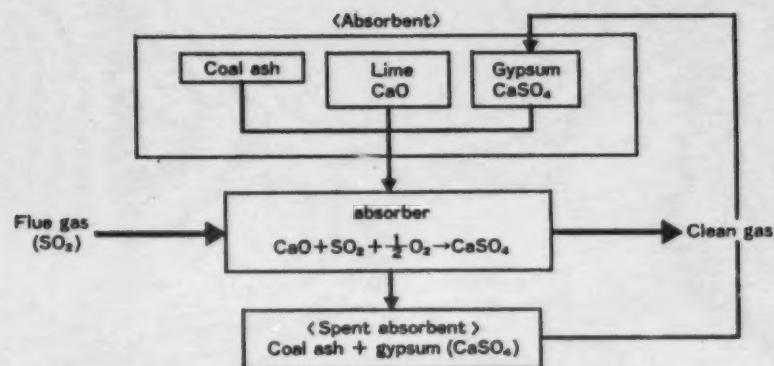


Figure 1. Principle of the process

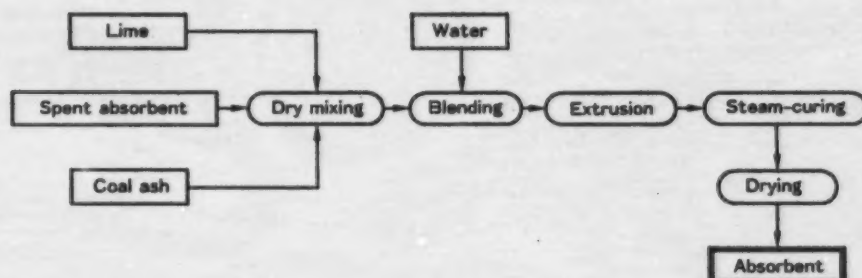


Figure 2. Standard flowsheet of absorbent production

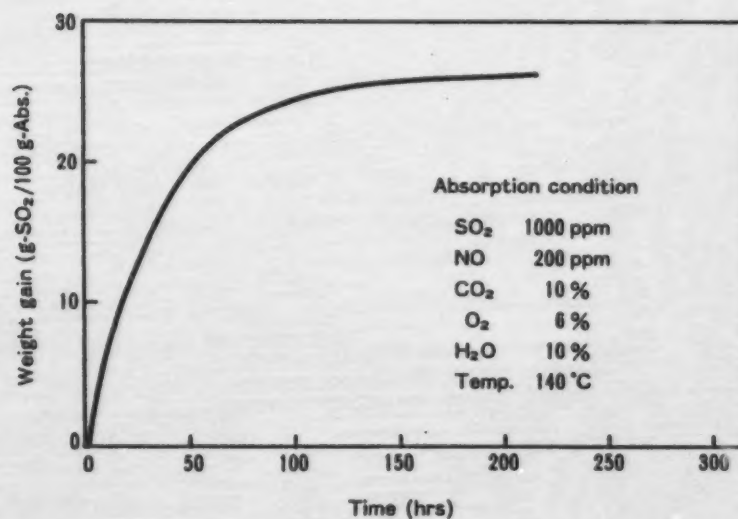


Figure 3. SO₂ absorption characteristics of absorbent

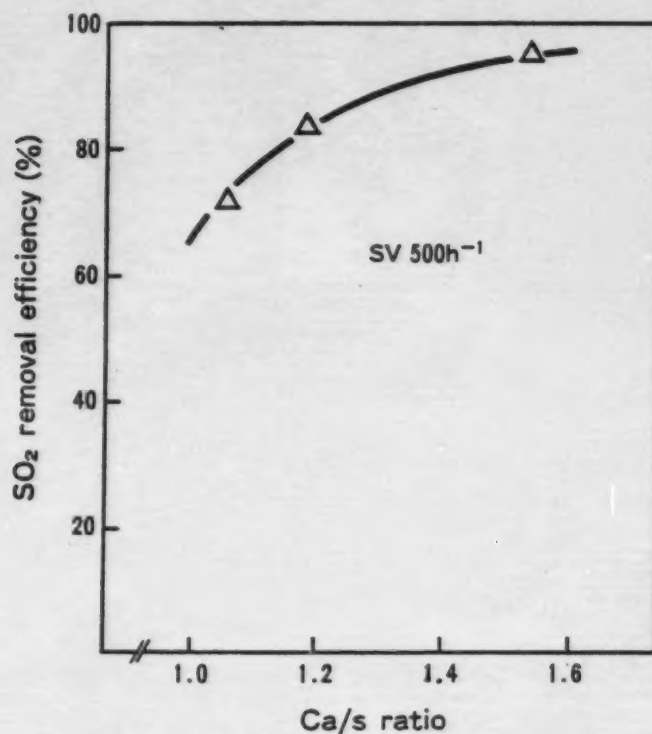


Figure 4. Relation between η_{SO_2} and Ca/S

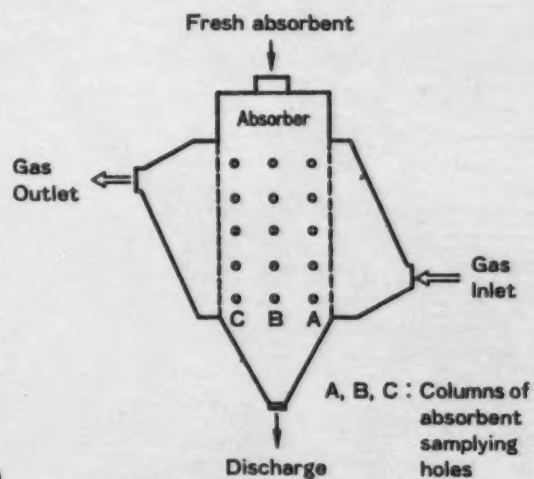
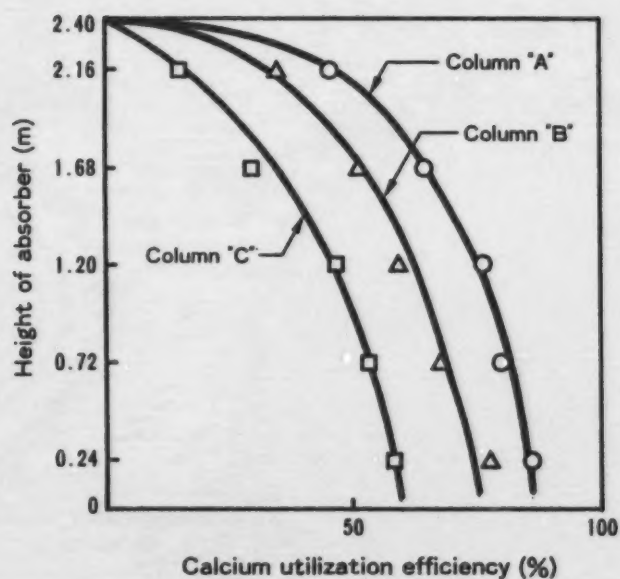


Figure 5. Calcium utilization efficiency of absorbent in the absorber

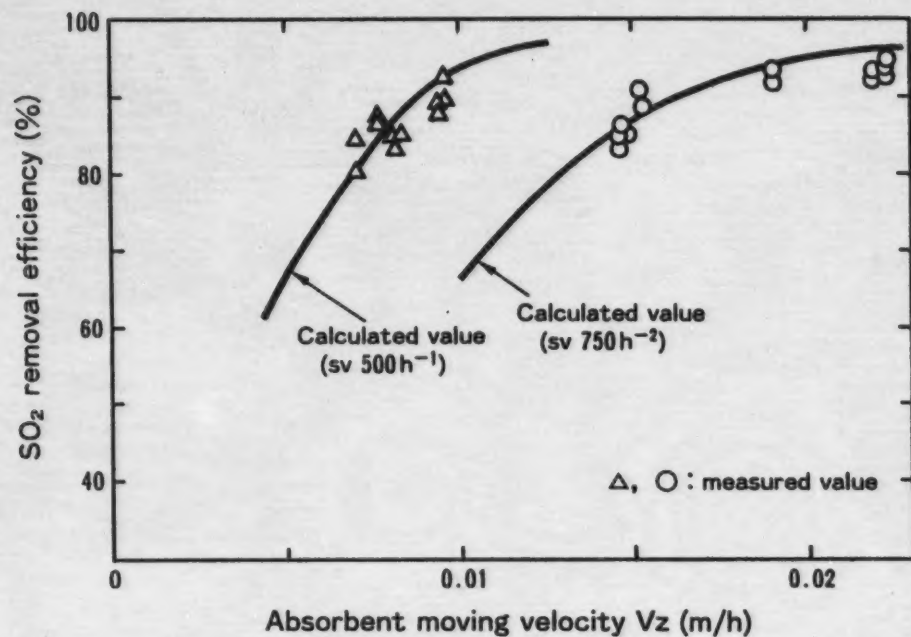


Figure 6. Comparison measured η_{SO_2} with calculated η_{SO_2}



Figure 7. Whole view of demonstration plant



Figure 9. Absorbent pellets

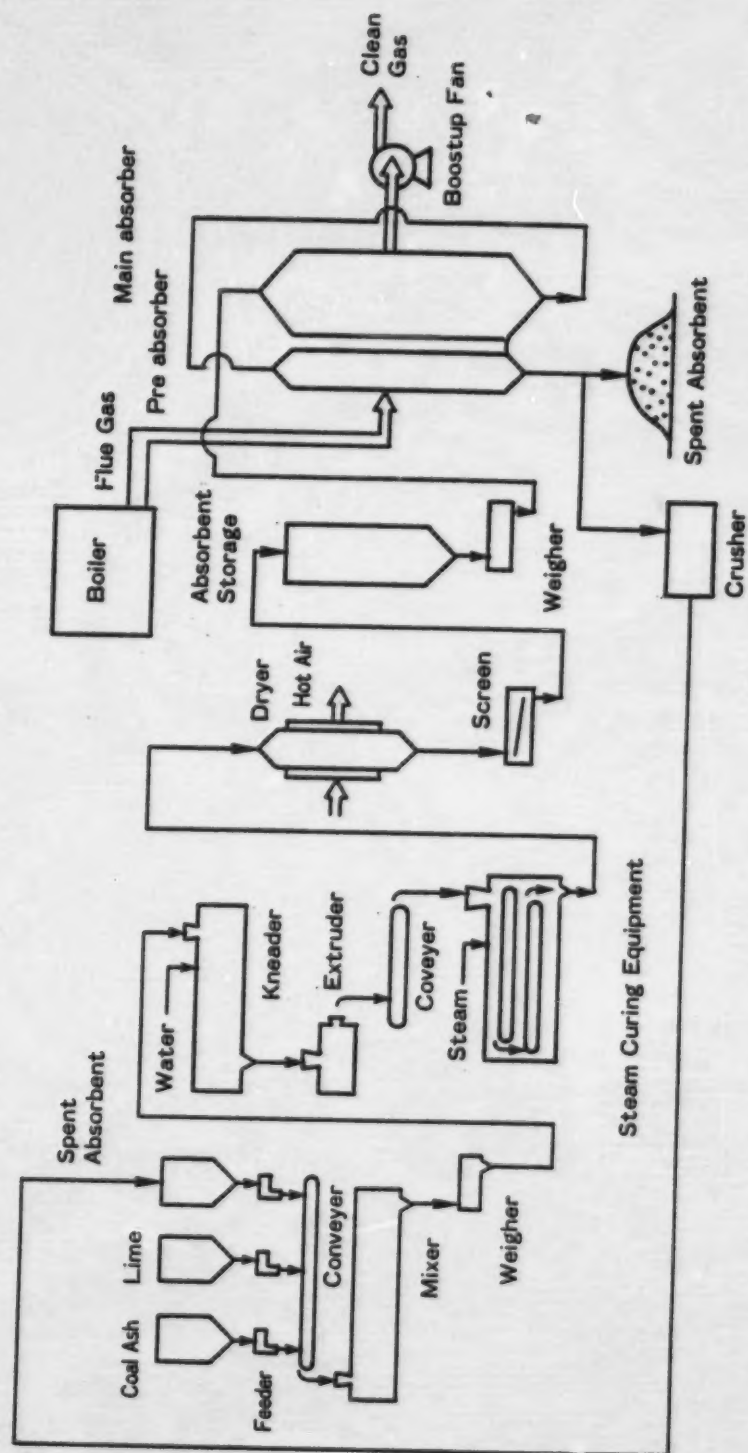


Figure 8. Flow sheet of dry FGD system using absorbent made from coal ash and lime

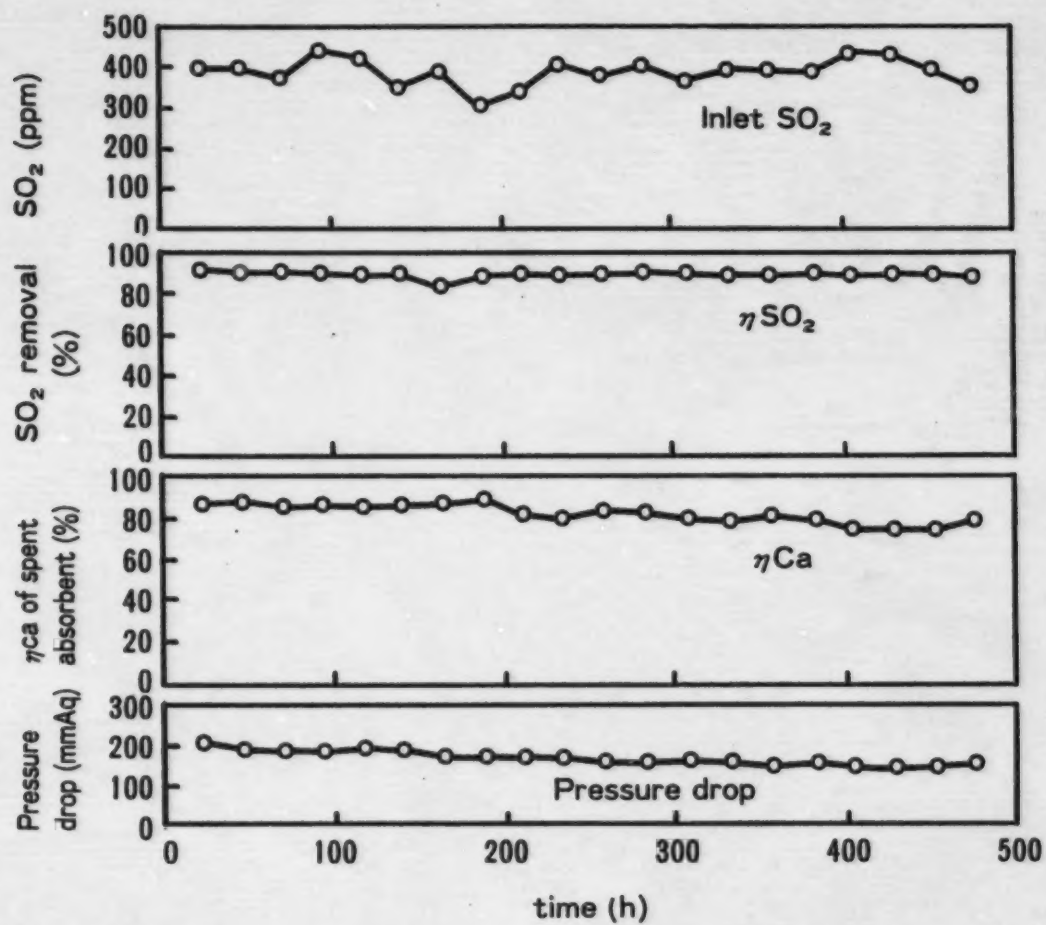


Figure 10. Absorption performance

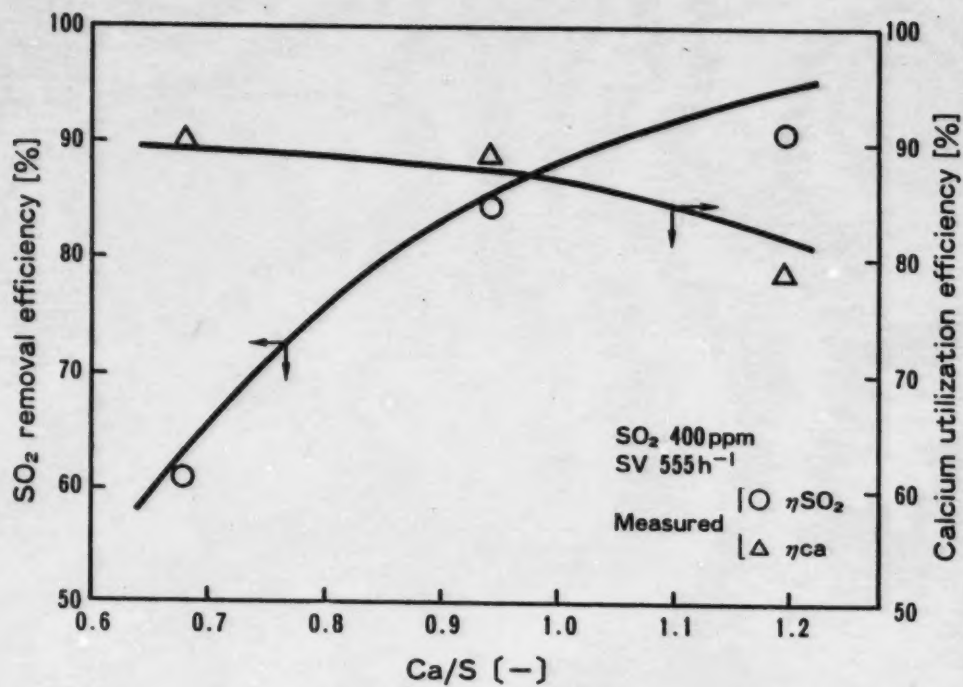


Figure 11. SO₂ removal performance

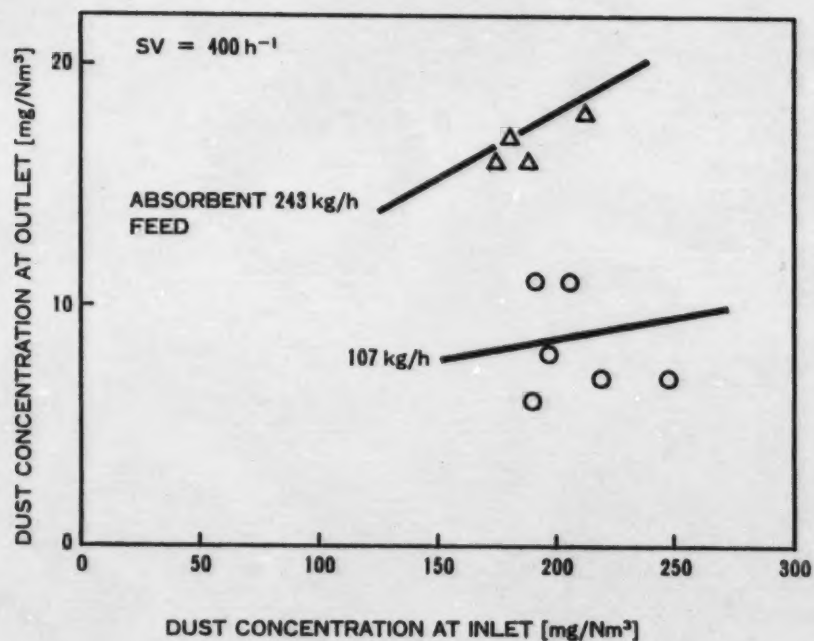


Figure 12. Dust removal characteristics

TABLE 1. FEATURES OF NEW PROCESS

	New process	Dry injection
Absorbent	Solid particle	Fine powder
Spent absorbent	Compound of fly-ash, gypsum	Calcium sulfite
Sulfur removal	90%	50—70%
Ca/S	1.05—1.10	3 — 5
Downstream treatment	Not required	Required bag house, cyclone
Attrition of boiler tube	No	To be considered

TABLE 2. EFFECT OF THE PRODUCTION CONDITION ON ACTIVITY

No.	Compn. of raw materials(%)			Water added(%)	Steam-curing time (h)	Conditions of thermal treatment	Properties of absorbent	
	Ca(OH) ₂	CaSO ₄	Coal ash etc.				Surface area (m ² /g)	Activity (%)
1	15	8	Coal ash 77	45	6	2h at 130°C	23	88
2	15	8	Coal ash 77	45	24	Omission	6	40
3	15	8	Coal ash 77	45	24	2h at 130°C	81	90
4	15	85	None	45	24	2h at 130°C	5	42
5	15	75	H ₂ SiO ₃ 10	45	24	2h at 130°C	13	78
6	15	75	Al(OH) ₃ 10	45	24	2h at 130°C	1	18
7	15	65	H ₂ SiO ₃ 10 (Al(OH) ₃) 10	45	24	2h at 130°C	27	64

The absorbent was prepared from the respective raw material paste, which contained gypsum (dihydrate) as a supply source for CaSO₄, by steam-curing, if necessary, followed by thermal treating. The activity was measured for the crushed material under the conditions: particle size of sample tested: 3.36-4.76 mm; gas compn.: SO₂ 1000 ppm, NO 200 ppm, O₂ 6%, CO₂ 12%, H₂O 10%, N₂ the balance; temp.: 130°C; reaction time: 50h.

TABLE 3. EFFECT OF THE KINDS OF COAL ASH ON ACTIVITY

Coal ash		A	B	C	D
Compn. of coal ash (%)	SiO ₂	61.4	46.1	67.0	56.5
	Al ₂ O ₃	24.4	27.8	23.0	22.4
	CaO	2.70	8.52	0.45	5.58
	MgO	1.71	2.54	0.38	1.04
	Na ₂ O	0.81	0.36	0.08	0.64
	K ₂ O	2.38	0.65	2.66	0.53
	Fe ₂ O ₃	4.79	6.84	1.51	3.26
	SO ₃	0.05	0.78	0.11	0.36
Activity of absorbent(%)		65/81*	81/99	74/98	82/99

* Time of activity test: 25h/50h. The test conditions except for reaction time are the same as those in the case of Table 2.

TABLE 4. EFFECT OF GAS COMPOSITION ON THE ABSORPTION OF SO₂

Exp. No.	Gas compn.*				Amount of SO ₂ absorbed(mg/g)
	NO	O ₂	CO ₂	H ₂ O	
1					132
2				N	67
3			N		166
4		N			77
5		N	N	N	57
6	N				57
7	N			N	38
8	N		N		79
9	N	N	N	N	36

Compn. of raw materials

Ca(OH)₂ 30%, spent absorbent 40%, coal ash 30%

Standard conditions for SO₂ absorption

Gas compn.: SO₂ 1000 ppm, NO 200 ppm, O₂ 6%, CO₂ 12%,
H₂O 10%, N₂ the balance

temp. : 130°C, reaction time: 6h

Particle size of sample: 1.7-2.5 mm

* N denotes the omission of the corresponding gaseous constituents.

TABLE 5. CASE STUDY OF ABSORBER

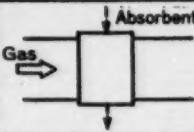
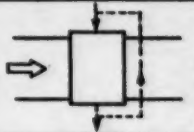
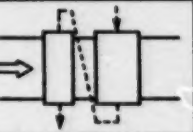
	Type- 1	Type- 2	Type- 3
Scheme			
SO ₂ in inlet gas (ppm)	550	550	550
Bed height (m)	15	15	15
Bed width (m)	4.7	4.7	4.7
SV (h ⁻¹)	400	400	400
Ca/S (-)	1.27	1.27	1.00
SO ₂ removal (%)	90	90	90
Absorbent utilization (%)	78.7	65.9	97.0

TABLE 6. SV VARIATION TEST

SV [h ⁻¹]	Ca/S [-]	Calculated		Measured	
		η_{SO_2} [%]	η_{Ca} [%]	η_{SO_2} [%]	η_{Ca} [%]
370	1.12	98	84	97~98	82~85
555	1.19	94	82	89~93	79~83
740	0.96	76	84	73~76	83~84

DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

HYDRATE AND PROCESS PARAMETERS CONTROLLING SO₂ REMOVAL DURING HYDROXIDE INJECTION NEAR 1000°F

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ABSTRACT

Recent work on the hydrate injection process near 1000°F for SO₂ control has focused on optimizing the hydrate and injection parameters to maximize SO₂ removal. The two sorbent characteristics that have the greatest influence on sorbent utilization are the initial hydrate surface area and particle size. Injecting hydrates with a mass mean diameter of about 1 μ m (measured by sedimentation) and surface areas ranging from 20 to 40 m²/g has produced conversions to CaSO_x as great as 60%. In-situ particle sizing, however, has shown that particles have a tendency to agglomerate as they travel through pipelines, yielding a coarser effective particle size and a lower utilization.

Other process parameters which can have a major effect on the sorbent utilization are the injection temperature, the initial SO₂ concentration, the Ca/S rate and the hydrate/flue gas mixing rate.

INTRODUCTION

The ability of hydroxides to react rapidly with SO₂ at temperatures below 1200°F was first noted in an earlier phase of the EPRI-sponsored Dry Sorbent Emission Control (DSEC) program when optimizing sorbent injectors on the KVB pilot facility. These tests showed that SO₂ capture levels with Genstar pressure hydrated dolomite decreased as the injection temperature was gradually reduced from 1800°F to approximately 1200°F but again increased with further reductions in injection temperature. This prompted a short study at the Southern Research Institute where Genstar pressure hydrated dolomite was injected at temperatures ranging from 2400°F to 200°F. As shown in Figure 1, a double hump behavior was observed, confirming that a second sulfation window existed between 1200°F and 800°F.

These initial encouraging results led to bench- and pilot-scale testing injecting hydroxides into temperatures between 800°F and 1000°F (1). These tests showed that the reaction rate of calcium hydroxide with SO₂ and CO₂ at around 1000°F was significantly faster than the reaction rate of CaO with SO₂ near

2000°F. The percentage conversion of the hydrate to either SO_2 or CO_2 was found to be determined primarily by the initial porosity of the hydrate. Hydrates with a high porosity showed total conversions to CaSO_3 or CaSO_4 greater than 70%. The sorbent utilization or fractional conversion of Ca(OH)_2 to CaSO_3 (on a molar basis), was found to be determined primarily by the initial porosity, particle size, SO_2 concentration, injection temperature and sorbent/gas mixing rate. In effect these parameters controlled the ratio of $\text{CaSO}_x/\text{CaCO}_3$ formed in the solid.

This paper reviews recent work investigating methods of enhancing hydrate reactivity with SO_2 near a reaction temperature of 1000°F and also discusses the effect of furnace parameters on the SO_2 removal.

MEASUREMENT EQUIPMENT

BENCH-SCALE REACTOR

Many of the experiments have been conducted in an electrically-heated, isothermal plug flow reactor (see Figure 2). Various gas compositions can be produced in a precombustor section upstream of the reactor. Either CH_4 or H_2 can be burned to produce flue gases with or without CO_2 . The temperature of the gas mixture can be adjusted by mixing in bottled gases (N_2 , CO_2 or air) or by adjusting the amount of insulation on the precombustor. Water can also be added to adjust the moisture content of the gases.

The gases leaving the precombustor are passed through several flow straightening devices before entering the electrically-heated reactor. The gas temperature at the reactor entrance is measured with a suction pyrometer. Velocity measurements obtained in the reactor have shown that a nearly plug flow profile is established and maintained over the length of the reactor. Temperature measurements inside the reactor, with an aspirated thermocouple, have demonstrated temperature axial and radial uniformity to $\pm 10^\circ\text{F}$.

Sorbent is fed with a screw feeder and injected with a radial sprayer to achieve rapid mixing at the top of the reactor. During the isothermal tests, the Ca/S ratio was nominally 1.0.

Solid samples are collected with an air quench probe which can be positioned at about 250°F. Tests conducted to assess possible reaction between the solid and SO_2 in the sampling system have shown that although reaction can occur, the utilization levels in the reactor are large compared to those occurring in the probe and filter. All isothermal data presented here are from analysis of solid samples for C, H, SO_3 and SO_4 . For these test results, the reactor gas composition was maintained at 3000 ppm SO_2 , 10 percent CO_2 , 4 percent O_2 , 15 percent H_2O and the balance N_2 .

PILOT-SCALE FACILITY

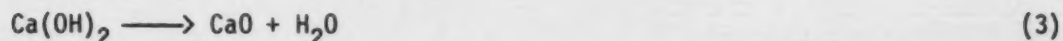
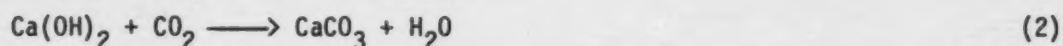
Other tests were also performed in a pilot scale reactor, fired on a 3% sulfur coal and set up to duplicate the 1000°F/s quench rate of a utility boiler between 1200°F and 800°F. The furnace is shown schematically in Figure 3. The upper furnace section is used to drop the gas temperature to 1200°F. The furnace diameter is then decreased to increase the velocity to obtain a reasonable spatial resolution with temperature. The correct temperature profile is produced by varying the number and position of convective cooling tubes placed into the lower furnace.

The sorbent utilization can be measured either by monitoring the ΔSO_2 with and without sorbent injection or by collecting solid samples.

During the pilot tests, the nominal flue gas composition was 5 percent O_2 , 14 percent CO_2 , 2500 ppm SO_2 , 7 percent H_2O and the balance N_2 .

PROCESS FUNDAMENTALS

Unlike the higher temperature sulfation window around 2000°F where CaSO_4 is the only thermodynamically stable compound, MgSO_4 , CaCO_3 and CaSO_3 are also stable species in the temperature range 1200°F - 800°F. As shown earlier (1), the amount of SO_2 capture will initially depend on the rate of three competing reactions:



Reaction (2) imposes the greatest limitation on the hydrate's ability to react with SO_2 , since CO_2 is very abundant, the carbonate formed is unreactive at these temperatures, and the reaction consumes porosity. Reaction (3) has both positive and negative effects on the sorbent's ability to remove SO_2 . Dehydration forms relatively unreactive CaO , reducing the amount of Ca(OH)_2 available for reaction with SO_2 . However, dehydration also opens up additional porosity, allowing greater utilization of the remaining hydrate.

Maximizing SO_2 removal by hydrates injected at around 1000°F requires optimization of both sorbent and process parameters. Two parameters appear to control the hydrate's ability to remove SO_2 . The initial sorbent porosity (or surface area) is a good indicator of the hydrate's ability to react with either SO_2 or CO_2 . Figure 4 shows isothermal reactor data at 900°F for a variety of hydrates having initial surface areas ranging from 10 to 70 m^2/g . Total utilization (CaSO_x and CaCO_3) increases dramatically with surface area up to about 40 m^2/g and more slowly thereafter. At 900°F significant decomposition does not occur, and the initial surface area (or porosity) correlates with the ability of the hydrate to react with either SO_2 or CO_2 . Both CaCO_3 and CaSO_3 have larger mole volumes than Ca(OH)_2 . Consequently as the hydrate reacts with either SO_2 or CO_2 , porosity and surface area are lost.

The second important hydrate characteristic for enhancing SO_2 removal is particle size. Because the chemical reaction rate is so fast, bulk diffusion of SO_2 (but not CO_2 , which has a concentration 30 times greater than SO_2) to the particle can be a controlling factor unless the particles are less than 5 μm MMD. Figure 5 shows the calculated bulk-diffusion-limited reaction rate as percent utilization occurring in 10 ms as a function of particle size. The rate even for 6 μm particles is quite fast (5 percent utilization in 10 ms, 50 percent in 100 ms), but, unlike the situation present during high temperature injection where CaSO_4 is the only stable species, the sorbent is also reacting rapidly to form CaCO_3 .

A bulk diffusion limit for SO_2 capture during 1000°F injection has important implications concerning sorbent properties for achieving high SO_2 removal efficiencies. Decreasing the particle size, keeping surface area constant, should shift the ratio of $\text{CaSO}_3/\text{CaCO}_3$ formed to higher values. Increasing

surface area without decreasing the particle size should decrease the ratio of $\text{CaSO}_3/\text{CaCO}_3$ by increasing the reaction rate with CO_2 .

Figure 6 shows the measured relationship between particle size, as measured by sedimentation, and the $\text{CaSO}_x/\text{CaCO}_3$ ratio found in the solid sample after a 0.1 second residence time at 1000°F in the isothermal furnace. As expected, the $\text{CaSO}_x/\text{CaCO}_3$ ratio increases with decreasing particle size.

EFFECT OF HYDRATION TECHNIQUES ON SO_2 REMOVAL

Various alternative hydration methods and additives have been used in an attempt to increase the hydrate porosity and/or decrease the particle size distribution. These hydration techniques include:

- o alcohol/water hydration
- o calcium lignosulfonate surfactant (trade name: "lignosite")
- o various types of dispersants
- o sodium additives
- o sugar additives
- o pressure hydration

The greatest enhancement in SO_2 removal was found using either alcohol/water hydration or calcium lignosulfonate additives (a reasonably low cost material). Particularly at lower temperatures (below 1000°F) sugar addition has also proven beneficial. Sodium additives and pressure hydration gave little or no benefit when injected between 800°F and 1200°F .

Figure 7 compares the results of isothermal sulfation experiments using two types of alcohol/water hydrates and a commercial hydrate. One alcohol hydrate is produced by using a ratio of water and alcohol which yields a dry product with a $45 \text{ m}^2/\text{g}$ surface area upon completion of the hydration process. The second alcohol/water hydrate, labeled SS, is hydrated using an excess amount of alcohol and must be dried after hydration is complete. Although the alcohol hydrates produced by this process generally have very high surface areas ($70\text{--}80 \text{ m}^2/\text{g}$), the drying process creates very small sticky particles which have a tendency to agglomerate.

As shown in Figure 7, the total utilizations, $\text{CaSO}_x + \text{CaCO}_3$, show the relationship expected between initial surface area and percent conversion. However, the conversion to CaSO_x for the SS alcohol/water hydrate was considerably lower than for the alcohol/water hydrate produced by dry hydration. The apparent reason for the poor performance with the SS hydrate is the tendency for the individual particles to agglomerate. These agglomerates will behave as large particles, favoring CaCO_3 formation, due to the diffusion limitation on SO_2 discussed above.

The dry alcohol/water hydrate did give a significantly higher utilization than the commercial sorbent (45% vs. 26%). The improved result with the alcohol hydrate can be attributed to both a greater initial porosity and a smaller particle size.

Figure 8 compares pilot scale results achieved injecting commercial hydrates and a hydrate made using a calcium lignosite additive. The hydrate made with the additive performed 25% better than the Longview and Colton commercial hydrates at a 1000°F injection temperature, and was less sensitive to temperature. Utilization with the additive was approximately 40% over a temperature range from 900°F to 1100°F.

The improved performance of the calcium lignosite additive hydrate is most likely due to the effectiveness of the surfactant in maintaining a small particle size after the small hydrate particles are formed (i.e. inhibiting agglomeration -- see Figure 9).

Figure 10 shows the effect on sorbent utilization of adding different concentrations of sugar to the hydration water. The sugar percentages shown in Figure 10 are relative to the weight of fully hydrated lime. Sugar addition gives the greatest increase in hydrate utilization at temperatures around 900°F. At 900°F the commercial hydrate had a utilization of about 18%, while the hydrate made with 11.3% sugar had a 40% utilization.

The data show that at 900°F, and perhaps at lower temperatures as well, the porosity generated when the sugar evaporates from the hydrate allows greater utilizations. At higher temperatures, when the sorbent utilization is limited primarily by CaCO_3 and CaO formation, sugar addition is not as effective.

The reaction rate of the 11.3% sugar hydrates tested are shown in Figure 11. Particularly at 900°F the sorbent is still reacting between 250 and 500 ms, perhaps due to the relatively slow evaporation rate of the sugar. At 1000 and 1100°F the reaction appears to be relatively complete within the first 250 ms. Thus sugar may be a useful additive if relatively large cavity (residence time $>0.3\text{s}$) is available in the boiler at about 900°F. Otherwise, properly prepared hydrates with calcium lignosite additive will probably yield better results.

Several other hydration additives, including commercial dispersants, sodium hydroxide and a pressure hydrate, were tested for their effect on SO_2 removal. Figure 12 summarizes these test results and shows that none of these alternative hydration processes gave significant improvements in the hydrate utilization.

Reduction of Particle Size

Another technique used to increase the hydrate utilization was physical reduction of the particle size distribution during injection. Two methods were utilized: on-line classification and milling. Due to flow rate constraints, the classifier was used on the bench-scale reactor, and the mill was used with the pilot scale furnace. As shown in Figure 13, the classifier gave an exit particle size distribution of about 1 μm MMD for both a commercial and an alcohol hydrate. The mill also reduced the amount of coarse particles in the commercial hydrate, resulting in a 2-4 μm MMD feed (depending on measurement technique).

Figure 14 shows the results of tests run with the Colton and an alcohol water hydrate over a range of initial SO_2 concentrations from 500 to 3000 ppm. Tests were conducted with and without on-line classification using a nominal Ca/S ratio of 1.0. A significant improvement in calcium utilization was achieved by using on-line classification. The greatest improvement in utilization was obtained for the Colton hydrate, where a factor of two to three increase in sorbent utilization was measured over the range of SO_2 concentrations tested. Significant improvement in the sorbent utilization by on-line classifying was

also obtained with the alcohol hydrate, and typically the alcohol hydrate gave slightly higher utilizations for an equivalent initial SO_2 concentration than the Colton hydrate.

Figure 15 shows the effect of injection temperature on the hydrate utilization injected through either the mill or eductor. The conventional hydrates injected using the eductor had a maximum utilization of 30-33% at a $\text{Ca/S} = 1.0$. The hydrate utilization for the milled sorbent was 40-45% and less dependent on temperature than when the hydrates were fed using the eductor. The hydrate made with the calcium lignosite additive gave equally high utilizations using either the mill or the eductor, indicating the additive was effective in producing a fine particle size feed.

Agglomeration Behavior

An additional hydrate characteristic which can be important is the agglomeration tendency in the transport line. In-situ particle size analysis was performed with a Malvern instrument at various locations along the transport line on a full scale (150 MW_e) installation, and in the KVB laboratory. The full scale feed system used a solids pump, which does little to de-agglomerate hydrate aggregates. Figure 16 shows the measured particle size distributions for a Steel Bros. and Linwood hydrate at several distances from the solids feeder. Initially the solids distribution showed a wide range of particle sizes with significant fractions both greater than 50 μm and less than 10 μm . However, as the hydrate traveled downstream, the large aggregates tended to break up into smaller size particles while the very fine fraction tended to agglomerate. After a long enough pipe length, in this case $L/D = 550$, the sorbent acquired a narrow size distribution, between 8 and 15 μm .

Similar measurements were taken on the 0.5×10^6 Btu/hr pilot scale furnace sorbent injection system. The high pressure eductor used to transport the solids was very effective in de-agglomerating the hydrate, producing a size distribution similar to that measured by sedimentation. As shown in Figure 17, mass mean diameter increased, suggesting that the fine particles agglomerated as they traveled downstream. The alcohol/water hydrate did, however, remain significantly finer than the other hydrates.

The Malvern particle size data indicate that an additional sorbent parameter should be considered agglomeration tendency in the transport system. Even though the hydrate entering the transport line may consist of very fine particles, if these particles coalesce in the line and are injected as large agglomerates, SO_2 removal will suffer. The SS hydrate's poor SO_2 removal rate may be due to this agglomeration tendency (Figure 7).

The Malvern data also suggests there may be some uncertainty in the earlier figures discussed in this paper which utilize sedimentation particle size data, particularly Figures 6, 7, 8 and 14. Although the trends shown for the effect of particle size on sorbent utilization are valid, the particle size distributions as injected are probably different than those measured by sedimentation. Particularly the fine particles created by classification or milling would be expected to have formed aggregates in the transport line increasing the effective particle size distribution relative to that measured after de-agglomeration of the bulk sample. Perhaps, if methods can be found for transporting 5 μm MMD commercial hydrates without aggregate formation in the line, high conversions to CaSO_x can be achieved without using additives or sophisticated hydration methods.

Furnace Variables

Furnace and injection system design and operation will also influence the sorbent utilization, and these parameters must be considered if optimum results are to be achieved. The most important system design parameters are:

- o injection temperature
- o initial SO₂ concentration
- o Ca/S ratio
- o mixing rate

The optimum injection temperature is between 950°F - 1050°F and varies with the initial sorbent surface area (porosity) and particle size. Hydrates which have a low initial porosity benefit the most from the porosity increase which dehydration creates and achieve maximum utilizations at temperatures slightly above 1000°F. Higher surface area hydrates give maximum utilizations at temperatures somewhat below 1000°F.

Small particles have been found to be less sensitive to temperature than large particles. Small particles form relatively high ratios of CaSO_x/CaCO₃, and consequently are not as sensitive to the changes in the carbonation rate, which is a function of temperature.

The initial SO₂ concentration has a direct effect on the bulk diffusion SO₂ reaction rate. Although the sulfation rate is still fast, even for low SO₂ concentration, the carbonation rate becomes equal or greater than the sulfation rate at low SO₂ concentrations. Figure 14 shows the effect of SO₂ concentration for two hydrate types and two particle sizes.

Figure 18 compares sorbent utilizations achieved with commercial hydrates at injection temperatures near 2200°F and 1000°F for Ca/S ratios ranging from 0.5 to 2.0. With a conventional hydrate and injection system, sorbent utilizations were similar for both upper furnace and economizer injection, with the utilization decreasing from 35% to 25% over the range of Ca/S ratios tested. When finer particles were injected, by on-line milling the Colton hydrate, the utilizations were higher over the entire range of Ca/S ratios tested, but still inversely proportional to Ca/S ratio.

The mixing rate that must be achieved to prevent a decrease in sorbent utilization also appears to be affected by the sorbent properties. To evaluate this effect, sorbents were injected under conditions that should yield different sulfation rates. The purpose of changing the sulfation rate was to confirm that the mixing rate would be the most important factor under the fast sulfation conditions needed to achieve good sorbent utilization. Fast sulfation conditions were established by using:

- o small particles - milled to about 3 μ m
- o high initial SO₂ level - 2500 ppm
- o high Ca/S ratio - 2:1

Conversely, slower sulfation rates were tested by using:

- o larger particles - unmilled Colton
- o low initial SO₂ concentration - 1000 ppm
- o low Ca/S ratio - 1:1

Results from tests conducted with three different mixing rates are shown in Figure 19. As expected, the mixing rate had the greatest influence on the sorbent utilization when the sulfation rate was fast and the Ca/S ratio was high. More importantly, high sulfation rates and rapid mixing between the hydrate and the SO₂ in the gas stream are needed to achieve high sorbent utilizations (>30%).

CONCLUSIONS

Several advancements have been made in producing reactive calcium hydrates for removing SO₂ when injecting into flue gas near 1000°F. This study showed that the greatest improvement in hydrate utilization is achieved by decreasing the sorbent particle size. Smaller particles may be obtained by either using additives in the hydration process or mechanically reducing the particle size during injection. Hydration additives that have shown the greatest benefit are alcohol and calcium lignosulfonate. By a combination of appropriate hydration processes and sorbent feed system, hydrates with the following characteristics should be produced to optimize SO₂ removal:

- o particle size: 2-3 μ m MMD
- o initial surface area: 20-40 m²/g

To achieve the benefits of high porosity and small size, the injection feed system should be located within 150 pipe diameters of the furnace injectors to avoid agglomeration in the transport lines. If the hydrate agglomerates, the aggregates will behave as larger particles and provide SO₂ removals that are similar to those obtained by upper furnace (~2200°F) injection.

If hydrate with the optimized characteristics are injected and rapidly mixed into the appropriate temperature regime, SO₂ removals should approach 45-55% at Ca/S = 1 and 70-80% at Ca/S = 2.

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This work was sponsored by the Electric Power Research Institute, and the authors would like to acknowledge the suggestions and support of Dick Rhudy and Mike McElroy during this program. Additionally, the authors appreciate the help provided by Dr. Larry Muzio, both in providing many of the hydrates used during these tests and for his many other contributions to the program.

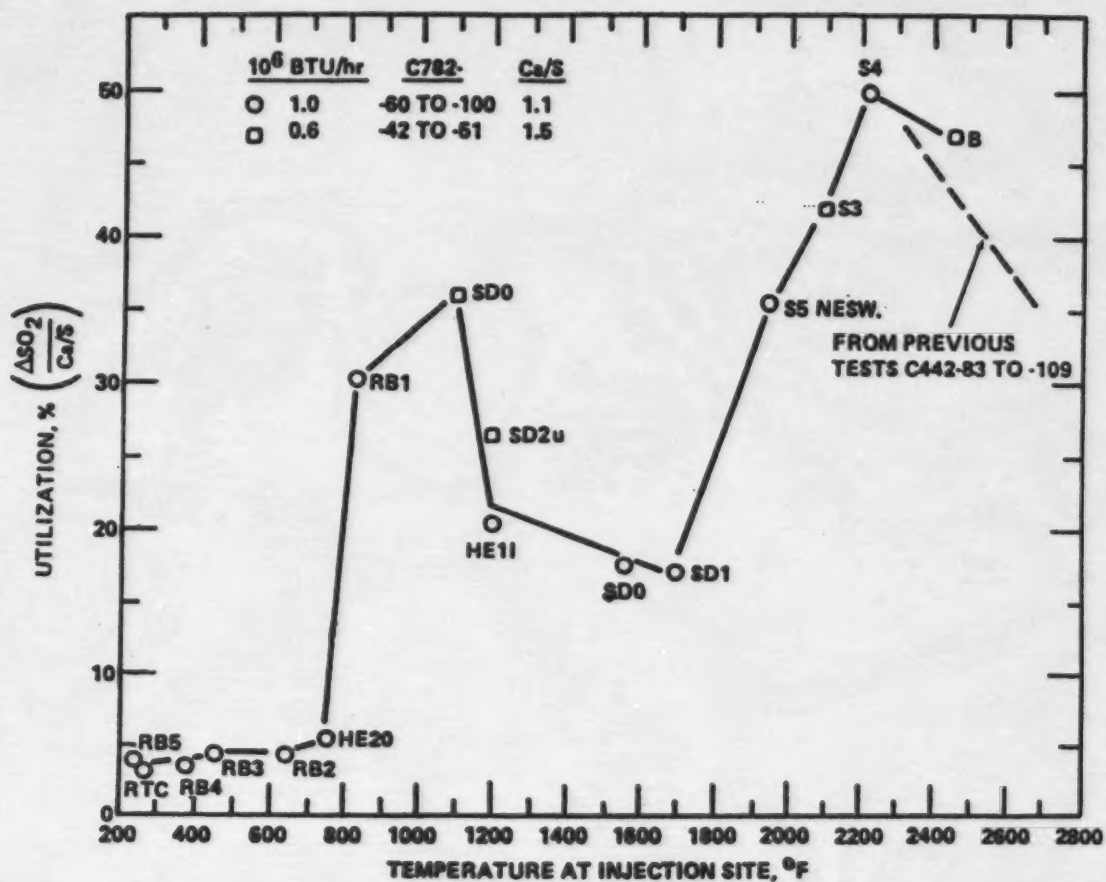


Figure 1. Utilization of Genstar PHDL over a wide range of injection temperatures, with coal firing. Injection sites noted for each point.

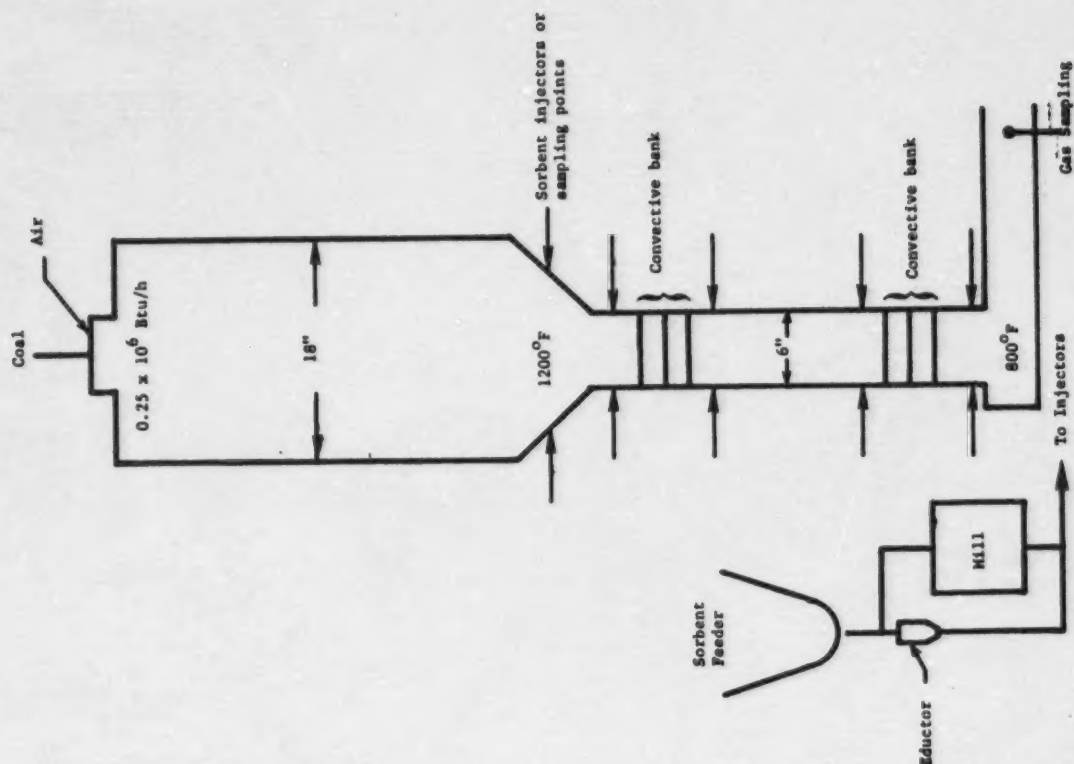


Figure 2. Configuration of bench scale reactor for low temperature sulfation studies.

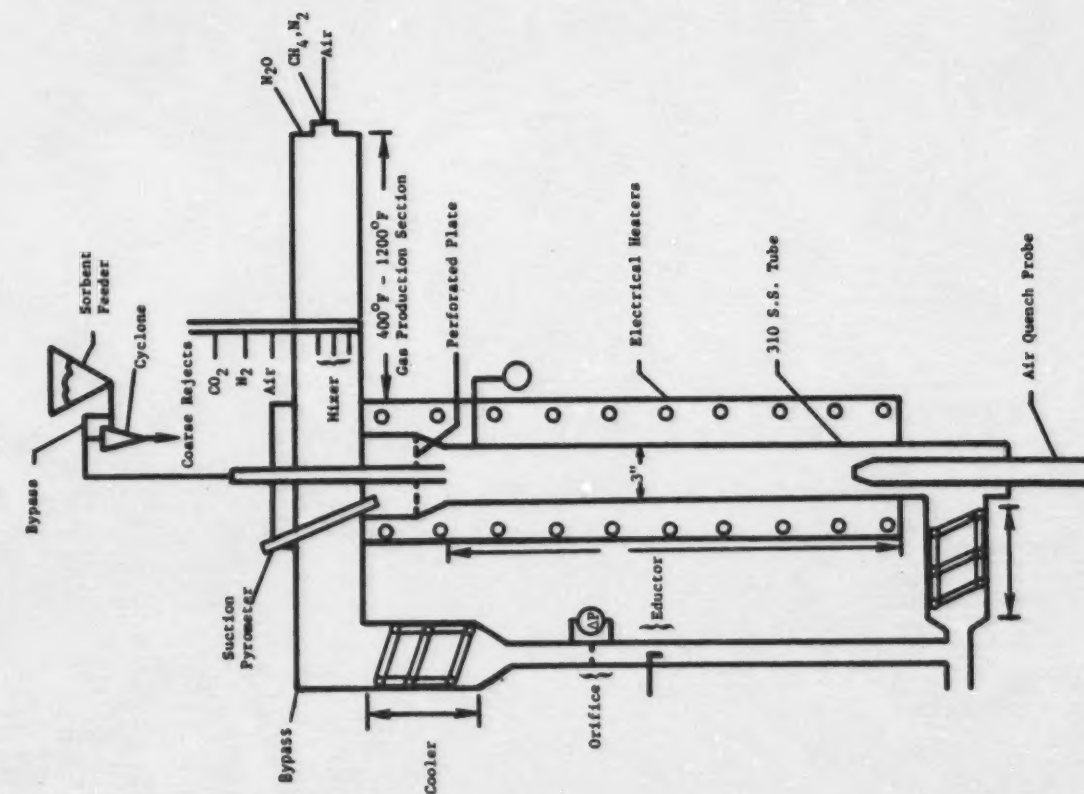


Figure 3. Pilot Plant Facility.

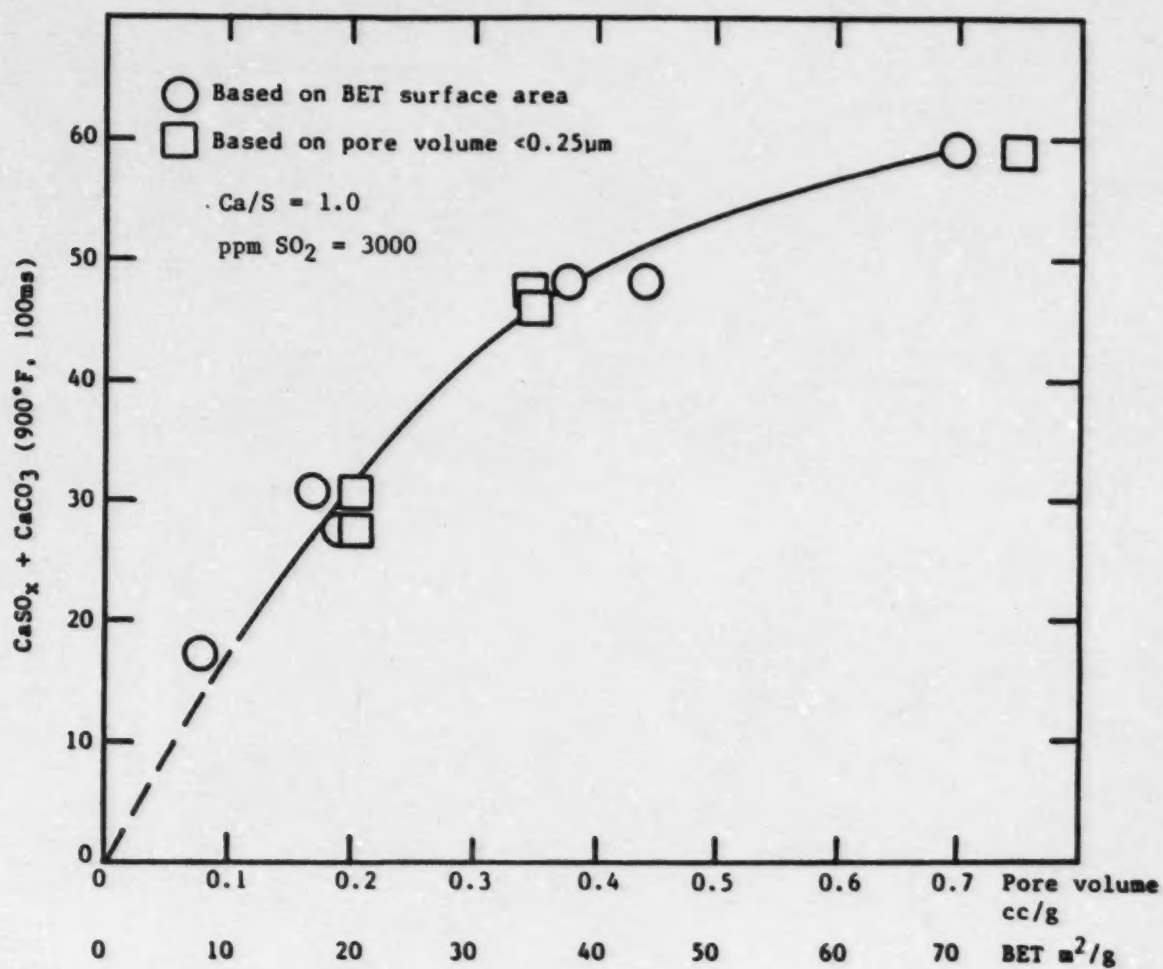


Figure 4. Relationship between total utilization and porosity for hydrates without additives (isothermal reactor).

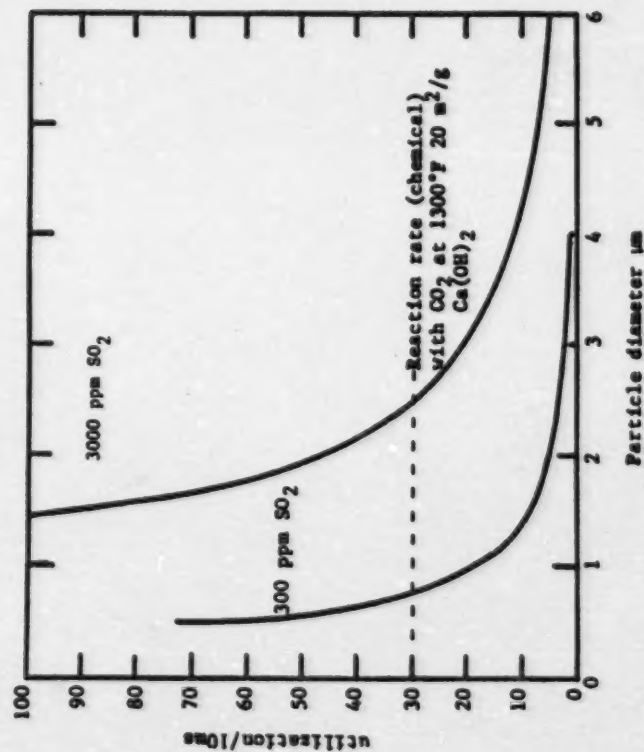


Figure 5. SO₂ reaction rate at 1000°F when limited by boundary layer diffusion.

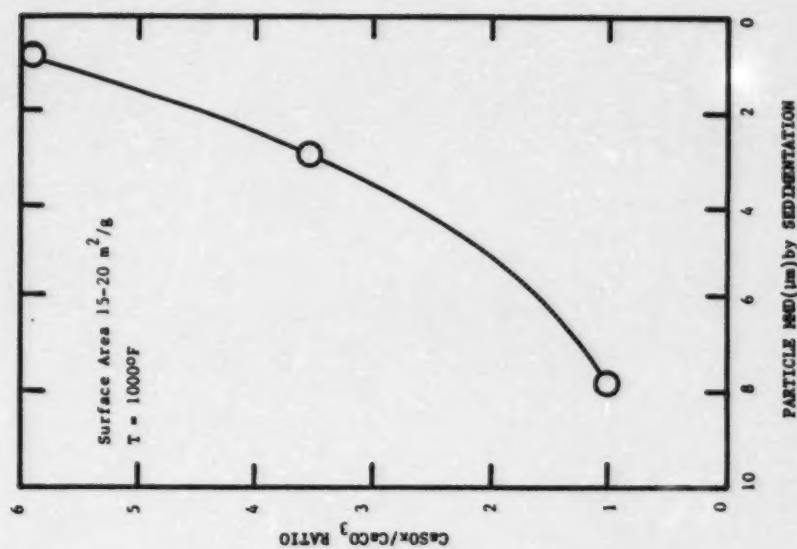


Figure 6. Measured effect of particle diameter on the CaSO_x/CaCO₃ ratio in isothermal reactor.

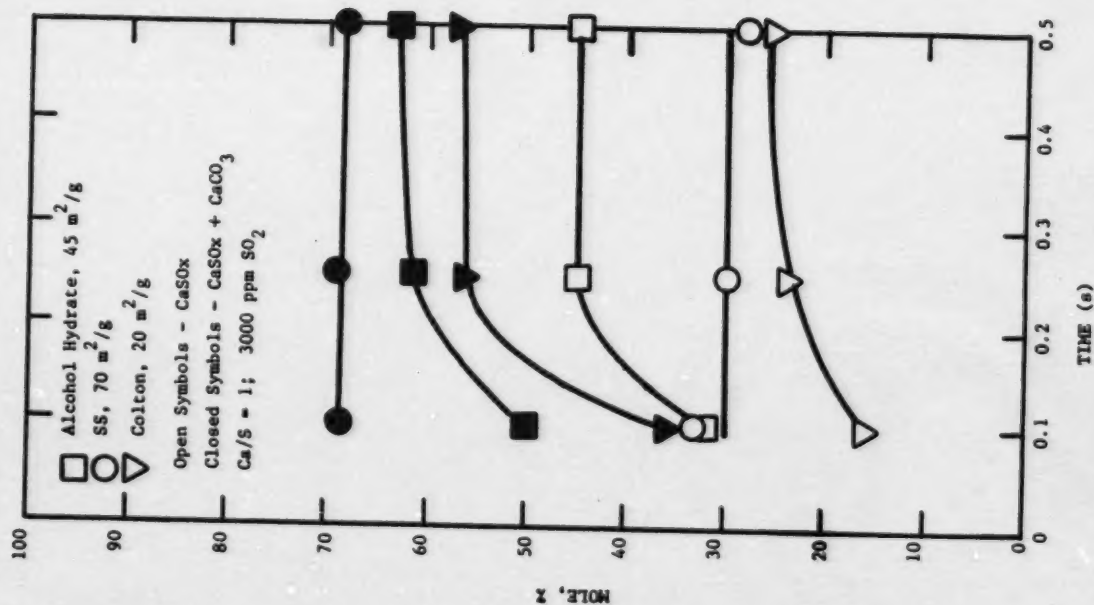


Figure 7. Comparison of alcohol/water and commercial hydrates, 1000F isothermal results.

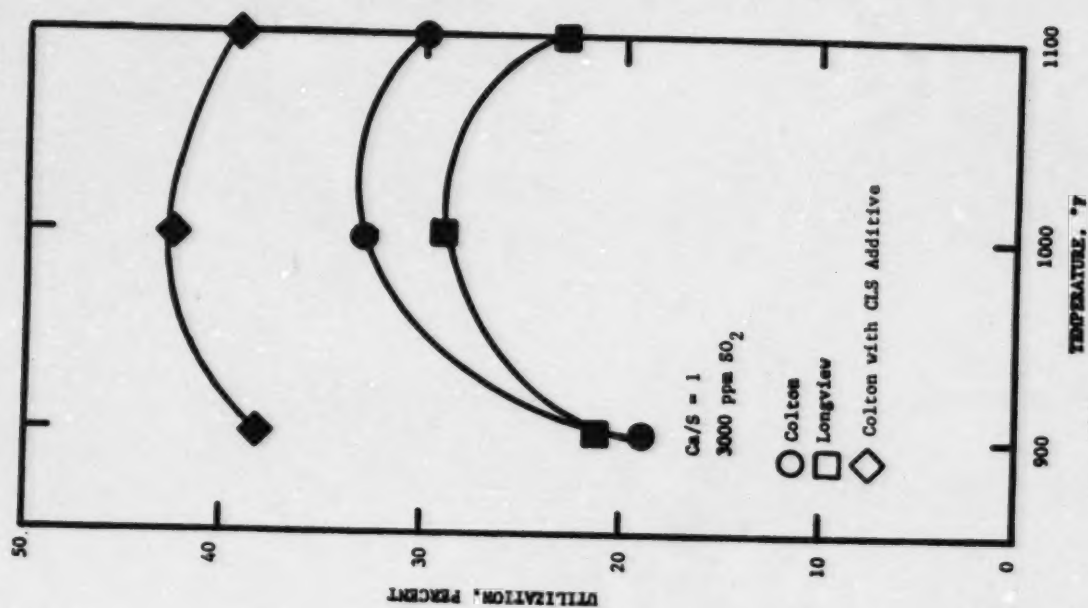


Figure 8. Effect of injection temperature for commercial hydrates with and without additives (pilot results with eductor feed system).

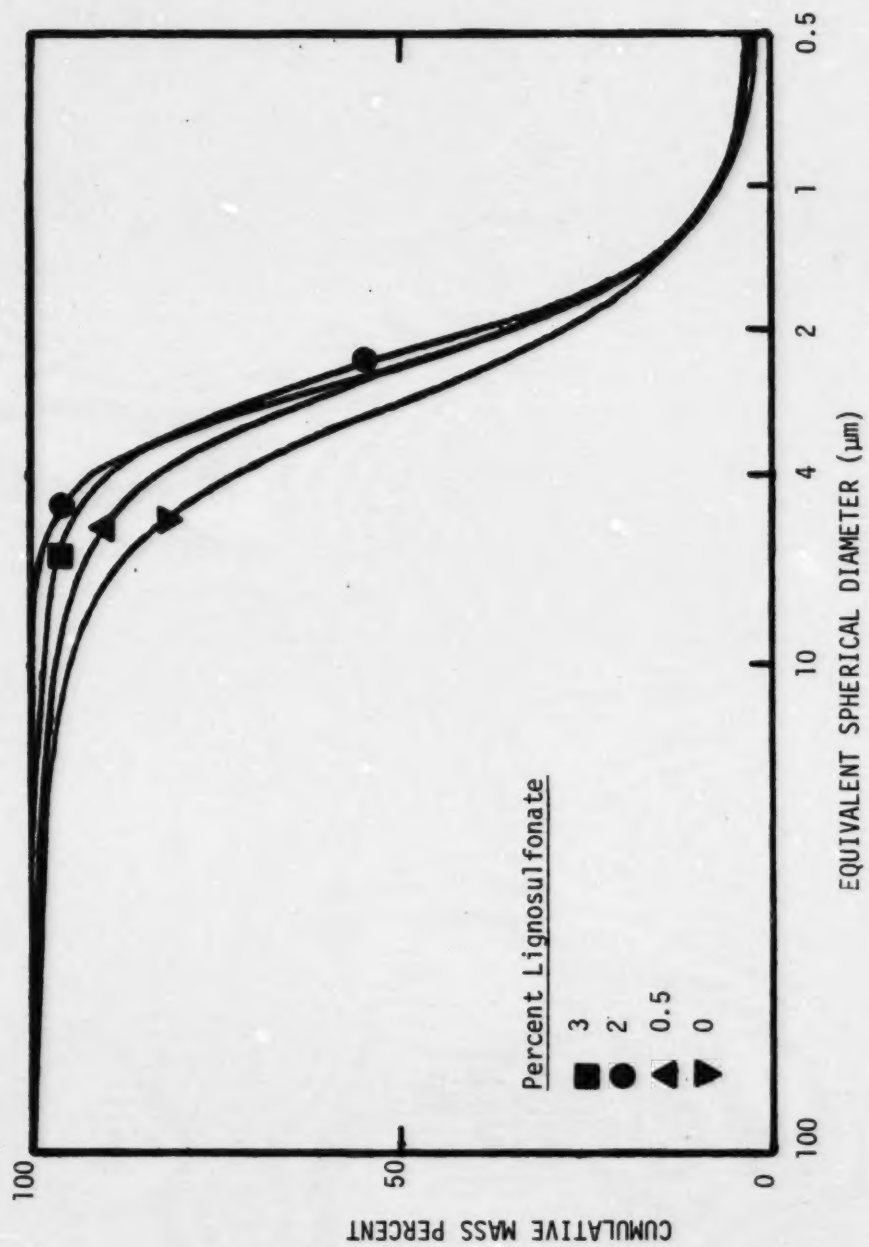


Figure 9. Size analyses of modified and unmodified hydrates by Sedigraph.

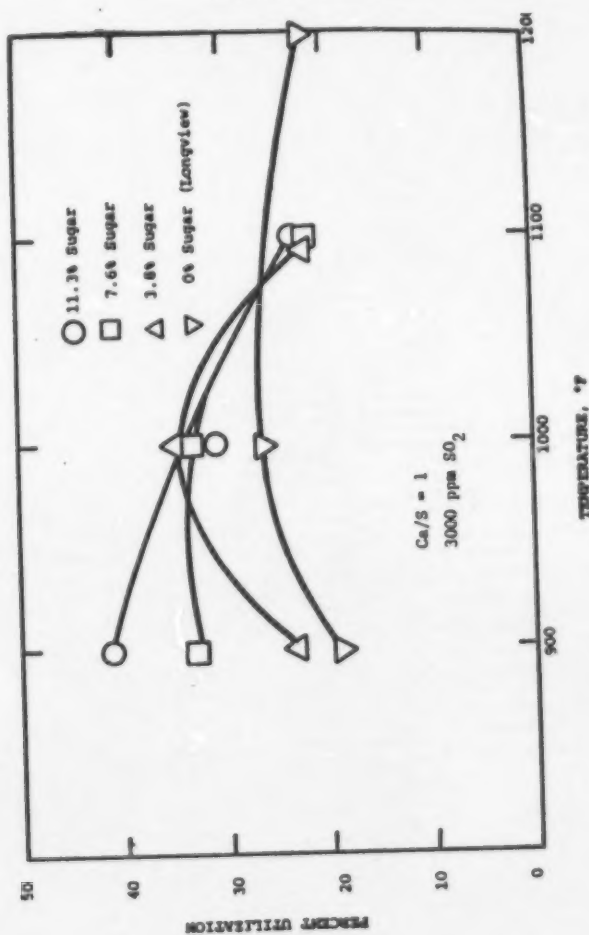


Figure 10. Effect of sugar content on the sorbent utilization after 0.5 s.

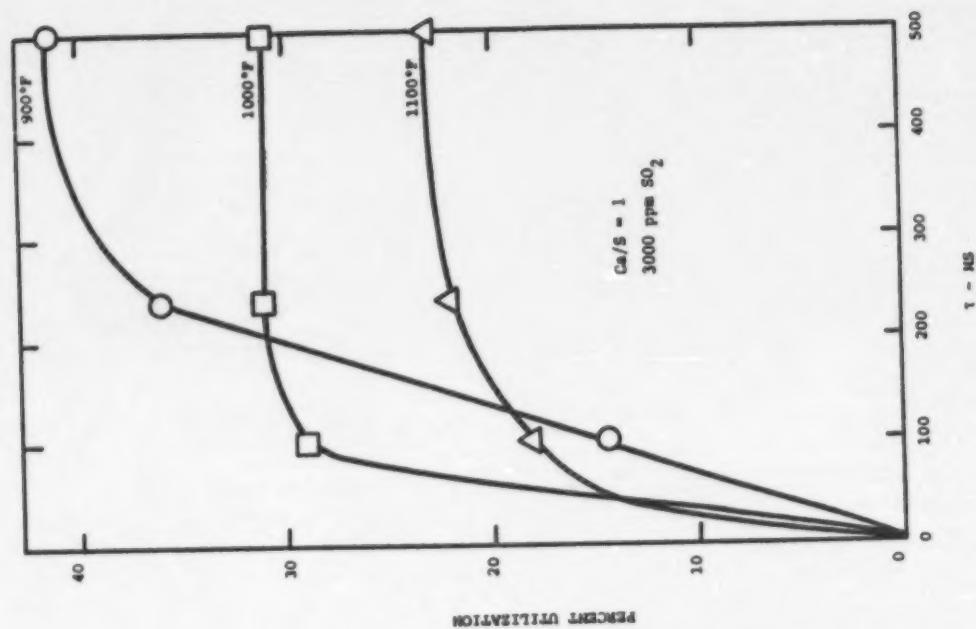


Figure 11. Reaction rates of the 11.3% sugar hydrate as a function of temperature.

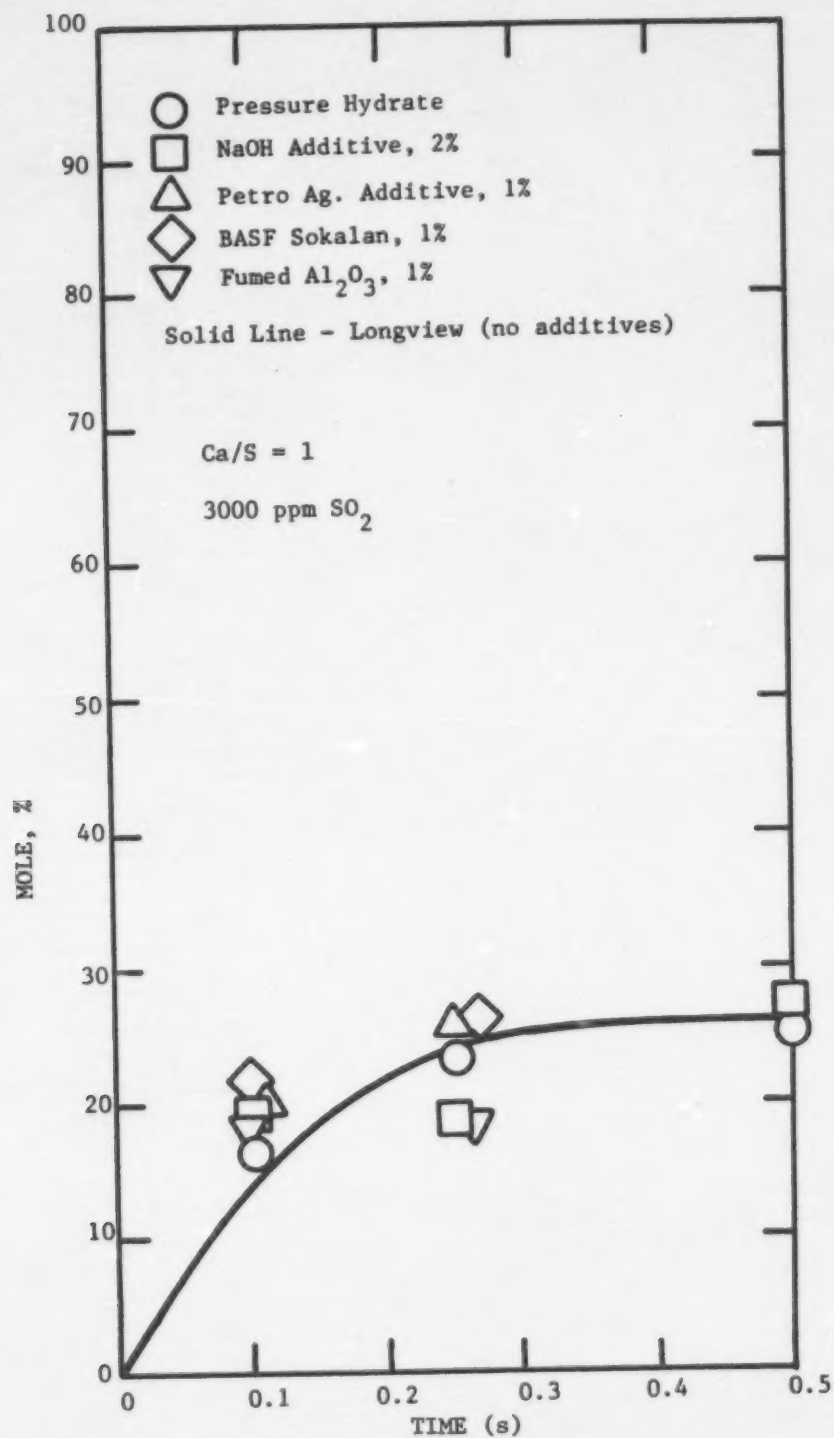


Figure 12. Effect of dispersant type additives, sodium, and pressure hydration at a 1000°F injection temperature.

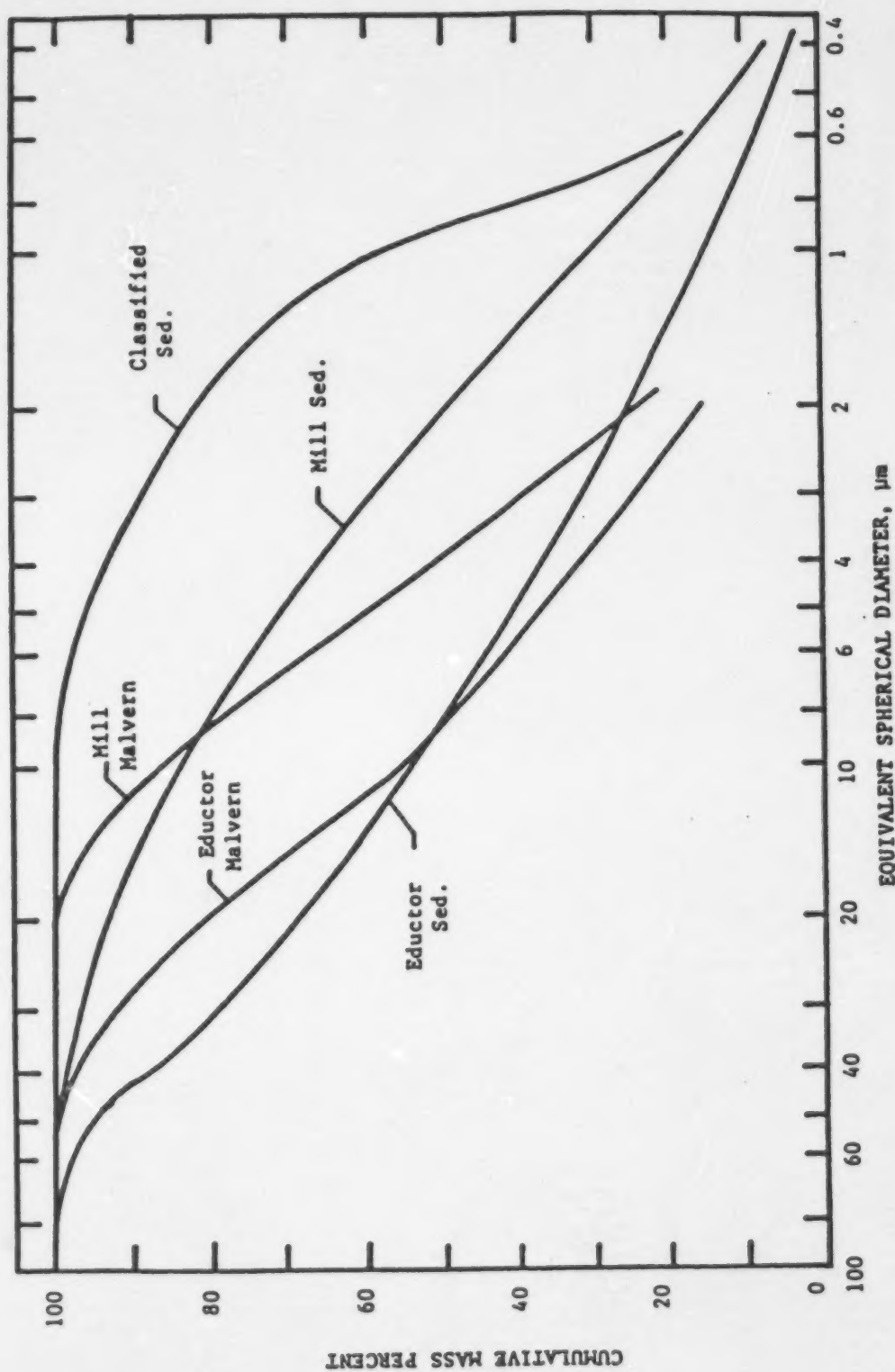


Figure 13. Size distributions of the different injection systems for the Colton hydrate, Malvern measurements at $L/D = 50$.

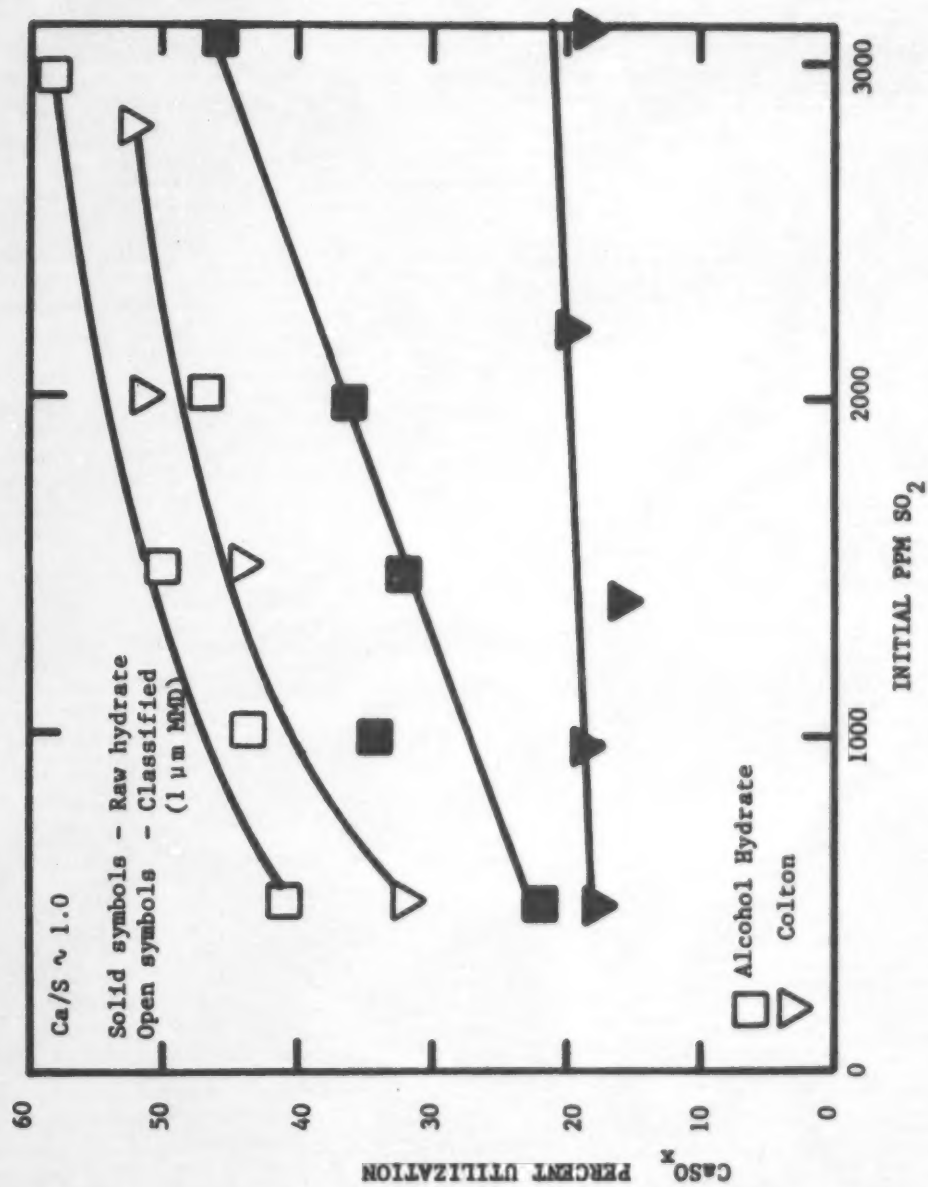


Figure 14. Comparison of on-line classification and raw hydrate injection (isothermal reactor, 1000°F.)

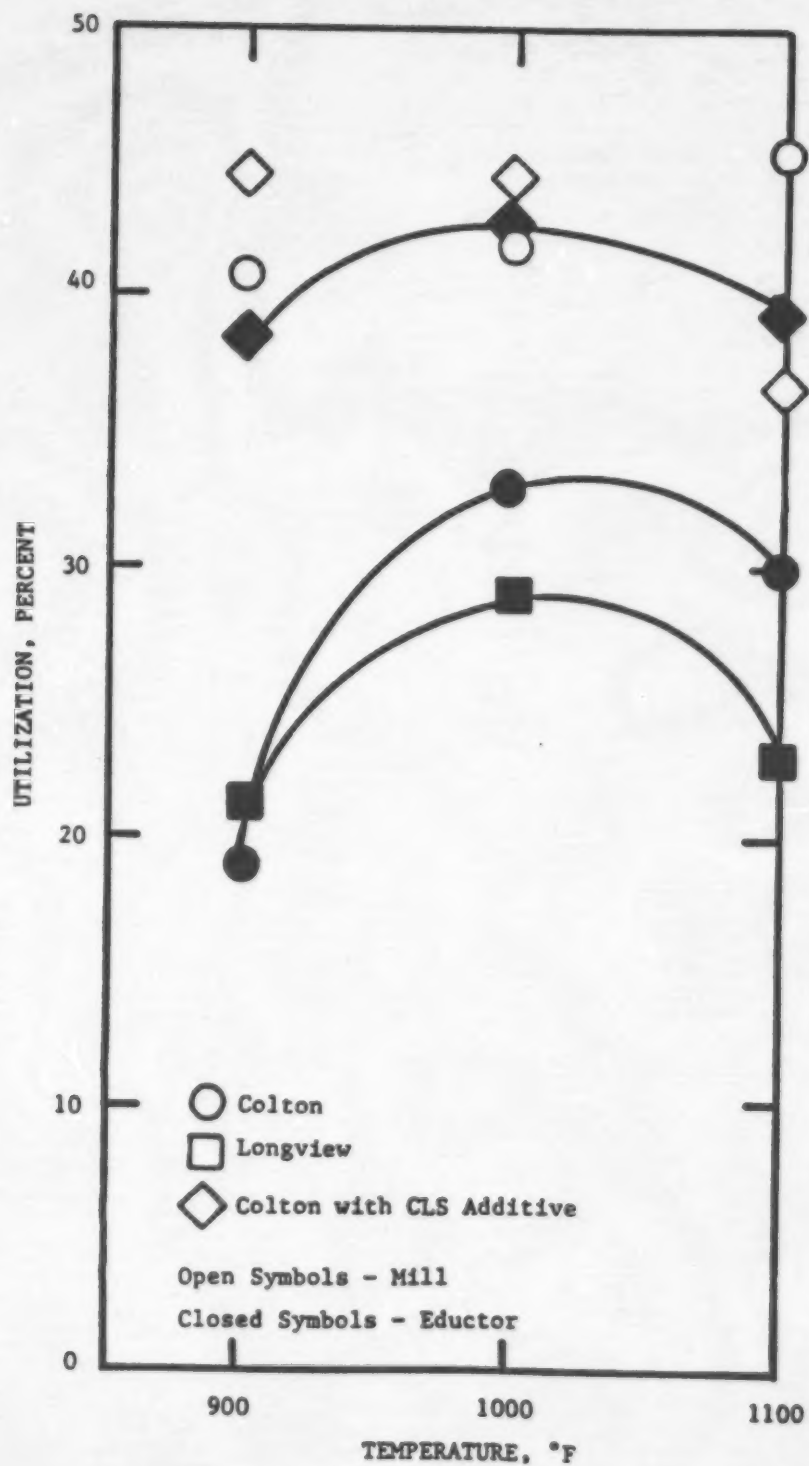


Figure 15. Effect of injection temperature for the commercial hydrates with and without additives, Ca/S = 1, SO₂ ~ 3000 ppm.

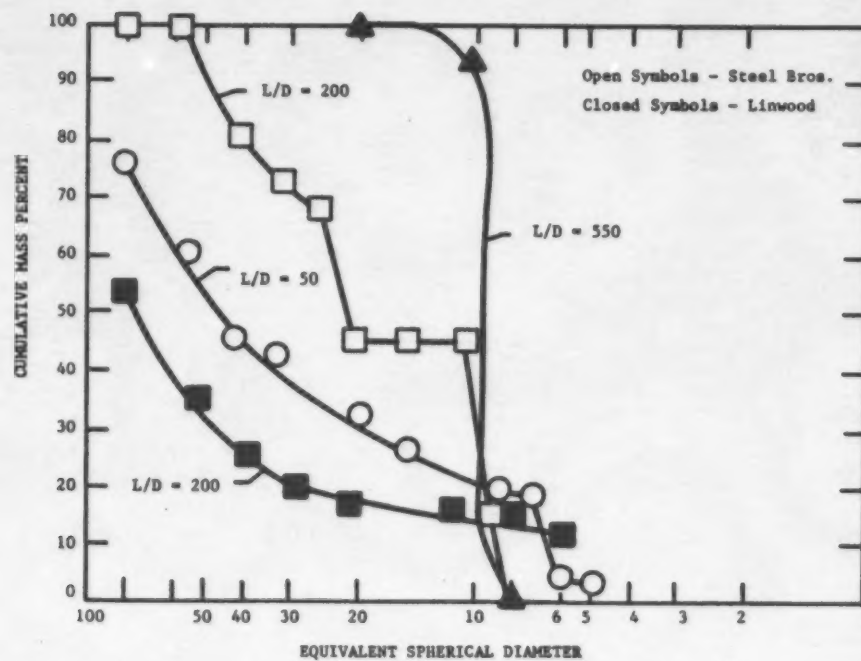


Figure 16. Comparison of measured particle size distribution at two sampling locations on a 150 MWe boiler.

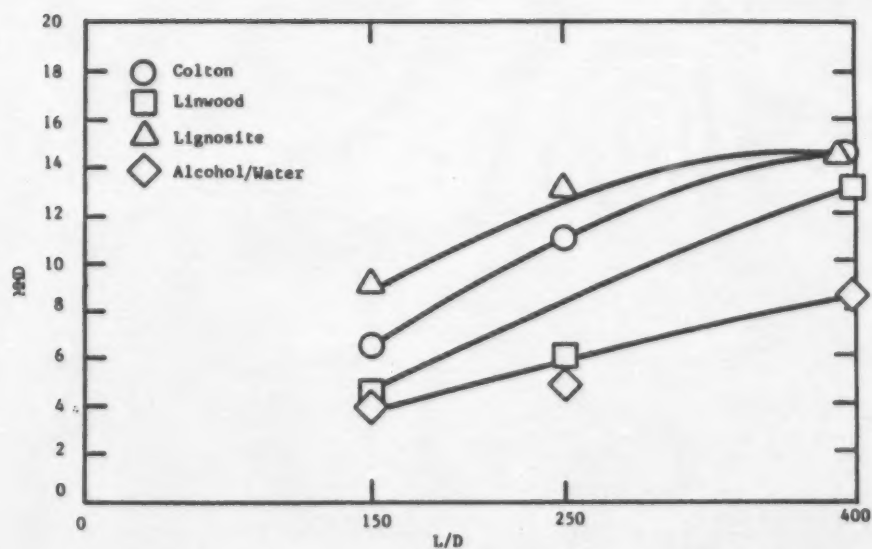


Figure 17. Mass mean diameter as a function of L/D (pilot furnace).

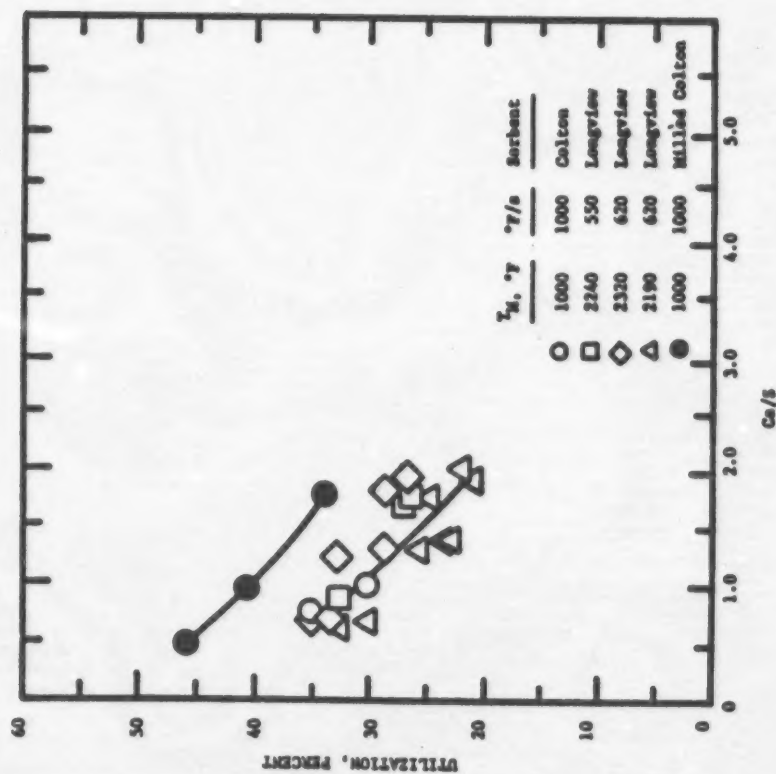


Figure 18. Utilization of Longview hydrate injected at different temperatures and quench rates with Hallmark coal.

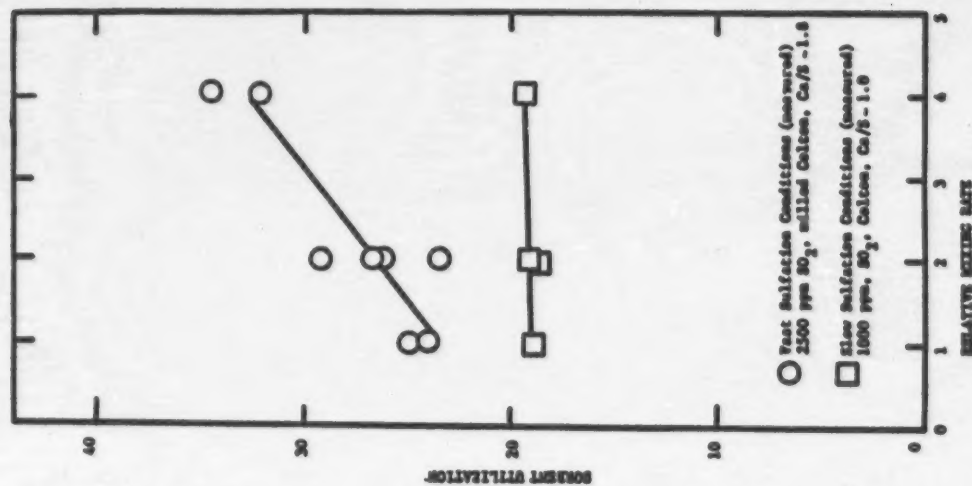


Figure 19. Effect of the relative mixing rate under fast and slow sulfation conditions.

E-SO_x PILOT EVALUATION

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ABSTRACT

E-SO_x is a proposed retrofit system that makes use of an existing electrostatic precipitator (ESP) for combined sulfur dioxide (SO₂) removal and particulate collection. The Ohio Coal Development Office, the U.S. Environmental Protection Agency (EPA), Babcock & Wilcox, and Ohio Edison are jointly sponsoring an evaluation of the process at a 5 MWe pilot on a flue gas slipstream from a utility boiler. A 10-month field pilot test program at the Ohio Edison R.E. Burger Station is scheduled to begin in early 1989. Small pilot experiments are described in which SO₂ removal and ESP performance were studied at conditions applicable to the 5 MWe pilot evaluation to establish performance and design criteria for a converted ESP. Preparations for the field evaluation are described and a status report of the field program is presented.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

E-SO_x is a retrofit process for coal-fired boilers, which combines in a single unit ESP technology for collecting particles and spray dryer technology for SO₂ removal. The process makes use of a modified existing ESP equipped with an auxiliary system for preparation and injection of a lime slurry into the ESP. E-SO_x is similar to other proposed retrofit lime- or limestone-dependent processes in that a dry solid waste is produced which is collected along with the fly ash in an ESP. The concept of E-SO_x offers an attractive option for acid rain mitigation. An economic evaluation of E-SO_x based on reasonable rates of SO₂ removal and lime utilization has indicated that it can be cost effective (1). The results of the economic study and the initial experimental results from EPA's laboratory study (2) gave impetus to further evaluation. As a result a cooperative effort by the U.S. EPA, the Ohio Coal Development Office (OCDO), and Babcock & Wilcox (B&W) has a goal of a 5 MWe pilot-plant evaluation of E-SO_x. The work reported here covers EPA and B&W experiments to verify assumptions used in predicting the cost effectiveness of E-SO_x, to characterize the process, and to describe the progress of field work. An earlier paper described the preliminary laboratory work (3), and detailed plans for the field evaluation were presented last year (4).

The goal of the E-SO_x field pilot test program is to obtain sufficient data to characterize the process and sufficient operating experience to demonstrate that this technology can be successfully applied at larger scale. The following specific goals have been set for the test program:

1. SO₂ Removal: Demonstrate that a minimum of 50% SO₂ removal can be obtained for coals with sulfur content typical of those burned at Ohio electric utility stations at economic stoichiometries.
2. Particulate Emissions: Establish and demonstrate suitable ESP configurations and/or modifications that will allow retrofit precipitators, modified for E-SO_x, to maintain their present particulate emissions.
3. Waste Product Disposal: Demonstrate that disposal of the solid waste product can be accomplished in an environmentally safe and cost effective manner.

In addition to these goals the field test program will acquire the necessary information to determine the cost of SO₂ reduction on a cost per ton of SO₂ removed basis.

In the E-SO_x retrofit concept shown schematically in Fig. 1, the front end of an existing ESP is converted to a spray chamber where contact is made between gaseous SO₂ and lime slurry droplets. Evaporation of the water also takes place in this converted section of the ESP so that the reaction product, excess lime, and fly ash that enter the remaining portion of the ESP are sufficiently dry for efficient ESP operation. The electrical components of the remaining ESP fields are left intact. To provide this contacting chamber with a sufficient space to allow a finite drying time of 1 second or greater, the ESP may typically lose 25 to 30% of its collector plate surface. At the same time, the particulate load will increase by a factor of three or more. This particulate, a large fraction of which is calcium based, has an extremely high electrical resistivity. The lime reaction with SO₂ will eliminate the effects of the sulfur trioxide (SO₃)

that would tend to lower this resistivity. On the other hand, lowering the gas temperature by the water spray will tend to more than compensate for resistivity increases due to ash composition. From the beginning, the E-SO_x concept has recognized the availability of advanced ESP technology to aid in maintaining the original particulate collection performance. Cooled pipe precharging, for example, can be introduced in retrofit ESPs to compensate for less collector surface or changes in resistivity characteristics.

The E-SO_x concept raises two fundamental questions which can be answered only by experiment. The first question concerns the feasibility of removing substantial SO₂ by contacting the rapidly moving gas with slurry droplets and drying the droplets within the space of one ESP section. The second question has to do with maintaining an acceptable level of ESP performance under a reduced collector area and an increased particulate loading. This paper is a progress report on experiments to address the questions and on design criteria developed to overcome problems inherent with the E-SO_x process.

EPA IN-HOUSE EXPERIMENTS

As shown in Fig. 2, the experimental setup in EPA's Air and Energy Engineering Research Laboratory consists of the ESP with electrical components removed from the first section and a venturi scrubber to remove excess SO₂ before the gas is exhausted to the atmosphere. Fig. 3 shows the layout of the 1000 acfm (28 am³/min) ESP. Outside air is heated to 149°C (300°F) prior to the injection of SO₂ to the desired concentration (usually 1500-2000 ppm) to simulate burning of moderately high sulfur coal. Fly ash is aspirated countercurrently into the simulated flue gas stream just before the cocurrent injection of the lime slurry. Slaked lime, containing 15-20% solids, is forced through a Casterjet two-fluid nozzle designed to provide an oblong spray pattern in the 1.27 m (50 in.) high x 0.38 m (15 in.) wide contacting chamber. The droplets, with a Sauter Mean diameter of typically about 30 μm, have a 1.5 to 2 s gas residence time in the chamber to evaporate most of the water. Evaporation effects a temperature drop, the magnitude of which depends upon the volume of water sprayed. The spray chamber is made up of the entrance section and the first of the four ESP sections. The electrical configuration of the remainder of the ESP can be varied. Cold pipe prechargers can be installed, if desired, between the first and second sections and between the third and fourth sections. Conventional wire electrodes of various diameters can be installed in all sections, except for the first. With the first section used as part of the spray chamber, the effective size of the ESP is reduced from 25 s/m (128 SCA) to 18.75 s/m (96 SCA). A number of experiments were run with the two prechargers installed, reducing the ESP to 12.5 s/m (64 SCA).

SO₂ REMOVAL TESTING

The primary objectives of the E-SO_x experiments carried out at EPA using the 1000 acfm modified pilot ESP were to verify E-SO_x as a competitive retrofit process for SO₂ removal and to determine the critical parameters which influence the degree of SO₂ removal. Once the critical factors were determined, they could be adjusted within limitations of the process to give the best conditions for SO₂ removal and sorbent utilization. To meet these objectives, experiments were planned to investigate impacts of indirect variables as well as those directly influencing the lime slurry/SO₂ reaction.

The flue gas SO₂ concentration is monitored at the ESP exit just before the gas leaving the ESP enters the venturi scrubber. A removal test requires 6 to 7

hours with about 4 hours of actual sorbent spraying. The remaining time is required for start-up in which the air flow, fly ash injection rate, and SO₂ delivery are adjusted for uniform gas flow through the ESP. At the end of the run, water spray replaces the slurry spray until once again there appears to be a steady outlet SO₂ concentration. The SO₂ concentration exiting the system is lower than it was originally because of the wall effects; i.e., unreacted lime deposited on walls and fixtures reacting with the SO₂ in the gas. These effects vary, but they will reduce in relative significance as the size of the ESP increases in scale-up.

Selection of Sorbent

E-SO_x utilizes a suspension of lime in water. Early experiments were conducted with a slurry of hydrated lime. However, the potential for attaining a smaller lime particle size though lime slaking resulted in a comparison between hydrated lime slurry and slaked lime at otherwise fixed conditions. Comparison of degree of removal is shown in Table 1. For a given approach to saturation at a constant stoichiometric ratio, the slaked lime performed better than the hydrate slurry. Similar results were obtained in experiments conducted by B&W. The improvement may be attributable to a difference in particle size or surface area. Brunauer, Emmett, and Teller (B.E.T.) surface area measurements showed the slaked lime about 30% higher in surface area. Since the use of slaked lime was preferred by virtue of cost as well as removal efficiency, most of the tests were conducted using slaked lime. Also in the economic study (1), the lowest cost scenario for E-SO_x made use of slaked pebble lime.

SO₂ Removal Dependence on Approach to Saturation and Calcium-to-Sulfur Ratio

A number of tests were performed in which only concentration and rate of injection of slaked lime were varied. In essence, this permitted an examination of the effect of the two most critical parameters on SO₂ removal: the temperature of approach to saturation (ΔT_{AS}) and the stoichiometric ratio of calcium to sulfur (Ca/S) in the slurry/gas mixing. When other parameters are held constant, including spray chamber geometry, gas flow rate, SO₂ concentration in the gas, and the inlet gas temperature, these injection parameters can be manipulated to give a ΔT_{AS} and Ca/S combination. There is a lower limit on ΔT_{AS} for adequate droplet drying and an upper limit on the solids concentration for consistent spraying. The fixed conditions are listed in Table 2.

The removal of SO₂ as a function of approach temperature for various stoichiometric ratios is shown in Fig. 4. This correlation between approach to saturation and SO₂ removal shows that good removal is possible at very low stoichiometric ratios, but only at very close approach temperatures. At these close approaches the droplets are not completely evaporated and excess moisture will pass into the ESP. The lower practical ΔT_{AS} is believed to be in the 15.6-16.7°C (28-30°F) range. Stoichiometric ratios of 1.3 to 1.4 produced a removal of 50% or better at a 16.7°C (30°F) approach to saturation. Results indicate a marginal improvement in SO₂ capture at a ratio of 1.4 but the increase in ratio with a smaller return makes the higher ratios less cost effective. The leveling off of removal rate with increasing Ca/S is also reflected in the plot of percent removal as a function of Ca/S in Figure 5.

Effect of Fly Ash on SO₂ Removal

In most of the EPA tests, fly ash was added as a component of the flue gas. However, similar tests were run without fly ash to determine if fly ash interferes with the E-SO_x process. A comparison of the runs with and without fly ash

at a given ΔT_{AS} and Ca/S is given in Table 3. Obviously a slight variation in either ΔT_{AS} or Ca/S has a greater effect than the fly ash. If there is a small SO_2 removal loss due to fly ash it can probably be compensated for by a small adjustment in one of the primary parameters.

Effect of Lower SO_2 Concentration

The E- SO_x process installation at the Ohio Edison plant site will be evaluated on emissions from burning 3-3.4% sulfur coal. EPA testing has concentrated on simulated flue gas streams containing about 2000 ppm SO_2 which corresponds to this coal sulfur. A limited number of tests were performed using 1500 ppm SO_2 , and plans are to look at 2500 ppm SO_2 . Data from the 1500 ppm tests are plotted in Fig. 6. Comparison of Fig. 6 with Fig. 4 indicates that somewhat better removal is achieved at 1500 ppm for a given ΔT_{AS} . At a 16.7°C (30°F) ΔT_{AS} and a Ca/S of 1.4, the removal runs about 10% higher at the 1500 ppm SO_2 level. The 50% removal goal was achieved in both cases.

PARTICULATE REMOVAL

The second fundamental question about E- SO_x as a retrofit concerns maintenance of an acceptable level of particulate removal. The question arises because of the reduction in SCA with a simultaneous increase in particulate loading. In conjunction with the SO_2 removal testing, the ESP electrical configuration was varied to determine effects of the increased load and change in characteristics of the particulate matter collected by the ESP. With sections 2, 3, and 4 energized and containing 0.32 cm (1/8 in.) wires, the ESP has an 18.8 s/m (96 SCA). With only two of the sections energized, the ESP was reduced to 12.5 s/m (64 SCA). Cold pipe prechargers, located between sections 1 and 2 and between 3 and 4, could be activated, but the SCA would remain the same. The data tabulated in Table 4 show that high mass efficiencies were obtained during a 4-fold increase in particulate loading and a 50% reduction in the SCA. There appears to be no significant change in efficiency with the amount of particulate as long as some moisture is present. The ESP emission rates in lb particulate/ 10^6 Btu (1 lb/ 10^6 Btu = 430.5 ng/J) as listed in Table 4 also indicate that, under E- SO_x conditions the ESP can meet or exceed the NSPS standard of 0.1 lb/ 10^6 Btu (43 ng/J). For fly ash only, the efficiency was reduced severely without moisture addition. In this case, the 38 kV could be maintained on the cold pipe precharger, but not on the wires because of back corona. Evaporation of water during the drying step lowers the temperature which accounts for the low resistivity of the lime sorbent/fly ash mixture in the E- SO_x process (3). As a consequence, back corona is not a problem.

It is evident from the data that the cold pipe precharger is not needed to lower the resistivity of the ash which is its primary function. However, the cold pipe precharger may still be needed in some retrofit systems to serve as an efficient collector for the small space that it occupies in the ESP.

EVALUATION OF A DROPLET IMPINGEMENT DEVICE

Experiments utilizing various laser diagnostics revealed that the atomized slurry stream severely disturbed the gas flow distribution to the ESP fields. Calculations using a drying (evaporation) computer model identified another limitation in the initial E- SO_x process design which must be corrected for successful application of the E- SO_x technology. Specifically the computer model indicated that insufficient drying time would result in unevaporated slurry droplets entering the charged ESP field. Utilizing their ESP performance

mathematical model, calculations by Southern Research Institute predicted that the non-uniform gas flow would produce unacceptably high particulate emissions from the ESP fields. B&W suggested that the installation of a Droplet Impingement Device (DID) (two staggered, vertical rows of pipe) may improve the velocity distribution as well as remove unevaporated slurry droplets from the gas stream.

The objectives of the DID evaluation were to:

1. Provide a uniform gas flow distribution to the ESP fields in order to maintain acceptable particulate emissions; i.e., the Industrial Gas Cleaning Institute (IGCI) standard that:
 - o 85% of the measured velocities be less than 1.15 times the average velocity.
 - o 99% of the measured velocities be less than 1.40 times the average velocity.
2. Minimize the unevaporated water droplets entering the ESP fields.
3. Characterize the potential for wetting the walls in the FGD chamber at various approaches to saturation temperatures.

Tests were conducted in the 1.8 x 1.8 m (6 x 6 ft) LIMB Humidification Facility. Figure 7 presents a schematic of the humidification duct and DID. Instead of lime slurry, water was sprayed into the duct using a 2x1 array (as shown in Fig. 8) of B&W I-jet MK-12 atomizers. The MK-12 atomizer has a nominal capacity of 3.0 l/m (0.8 gpm) and will be used in the E-SO_x field pilot. Gas velocity traverses were used to characterize the flow re-distribution performance of the DID. To improve the uniformity of the velocity distribution of the gas stream entering the simulated ESP field, several other flow correcting devices were also evaluated in combination with the DID. This included a perforated plate of uniform porosity, vertical baffles, horizontal stiffeners, deflectors, and a perforated plate with non-uniform porosity.

The DID was tested at several pipe spacings (corresponding to 30, 40, and 50% open area for one row of DID) and at two locations: 2.8 and 4.75 m (9.2 and 15.6 ft) downstream of the atomizers. The DID was generally effective as an unevaporated droplet removal device. Visual observations noted only minimal water penetration into the simulated ESP field with the 30 and 40% open area DID. Some water droplet penetration was observed at a 50% DID open area.

Laser obscuration measurements before and after the DID (50% open area and 2.8 m downstream of the atomizers) confirmed the visual observations. Fig. 9 summarizes the laser obscuration measurements and plots the percentage of water remaining in the gas stream both before and after the DID. The DID effectively reduced the concentration of unevaporated water droplets. The amount of unevaporated water slippage into the ESP increases only slightly with decreasing approach-to-saturation. Below a 22.2°C (40°F) approach-to-saturation, the water concentration at the DID inlet could not be accurately measured because of the excessive number of water droplets present.

The DID also improved the gas flow distribution into the simulated ESP field. Figures 10 and 11 are the normalized velocity contour plots for the gas flow distribution 30.5 cm (12 in.) before the DID (30% open area) and after the DID, 0.61 m (2 ft) into the simulated ESP field. The velocity distribution before

the DID was high in the center with negative values at the top and bottom. Smoke tests confirmed that gas recirculation existed at the top and bottom of the duct. The velocity profile in the ESP field downstream of the DID was the "mirror image" of the DID inlet. The gas velocity was lowest in the center and highest at the top and bottom. This is the "classic" case of overcorrection or too much restriction of the gas flow. The standard deviation improved from 2.38 on a normalized basis before the DID to 0.45 in the simulated ESP field. However, the DID alone did not correct the non-uniform gas flow sufficiently to satisfy the IGCI criteria. The V/V_{avg} profile in the ESP field contained 64% of the data points less than 1.15 and 83% less than 1.40.

Several flow correction devices were evaluated along with the DID. Emphasis was placed on devices with minimal horizontal surface area and which could be easily cleaned using conventional techniques such as sootblowing and mechanical rapping. The IGCI standards were achieved at both DID locations (2.8 and 4.75 m) with similar flow correction designs. Velocity contour plots for the flow distribution are plotted in Figs. 12 and 13. Fig. 14 is a schematic of the design that achieved the IGCI criteria at 2.8 m. The flow distribution for the 4.75 m run was slightly improved compared with the run at 2.8 m. The percent less than 1.15 times the average velocity was 96% compared with 86% at 2.8 m. For both of these runs, there were no data points above 1.40 times the average velocity. The standard deviation was 0.098 (at 4.75 m) compared with 0.148 (at 2.8 m).

With DID located 2.8 m downstream of the atomizers, a 27.8°C (50°F) approach-to-saturation was the lowest approach that could be achieved without severe unevaporated water droplet impingement of the DID. At a 27.8-28.9°C (50-52°F) approach, puddles of water would form at the base of DID, but could be removed with small drain holes. At lower approaches severe impingement of the DID occurs and the water on the floor could not be removed fast enough. Based on a drying time model, the extent of evaporation before the DID was only 90.5%. A minimum of 95% evaporation may be necessary to obtain dry, free flowing solids in the E-SO_x field pilot when atomizing lime slurry. To achieve a 16.7°C (30°F) approach, a DID location of about 4.6 m (15 ft) was necessary to achieve about 97% evaporation.

Because of the location of existing equipment in the humidifier, a DID location of 4.75 m downstream of the atomizers was chosen to conduct additional tests. At 4.75 m, a 16.7-17.8°C (30-32°F) approach appeared to be the lowest approach that could be continuously operated at without significant amounts of water collecting at the base of the DID. The unevaporated droplets were minimal and are not expected to be a concern in the E-SO_x field pilot. At a 15.6°C (28°F) approach, the unevaporated water droplets impinging onto DID increased dramatically.

The wall wetting potential was determined to be minimal and not a cause for concern. Moisture indicators were placed on the side walls upstream of DID. For all of the runs, including low approach-to-saturation temperatures, wall wetting was minimal. Some wetting of the windows (used for laser obscuration measurements) just upstream of the DID was observed at low approach-to-saturation. Because the DID acts as a flow distribution device, some of the gas flow will impact the side walls just before the DID. With the DID 2.8 m downstream of the atomizers, some wetting was observed at an approach of 27.8°C (50°F). At 4.75 m, wetting of the window did not occur until a 16.7°C (30°F) approach.

FIELD EVALUATION

In the E-SO_x 5 MWe field pilot, the DID will be evaluated at several distances from the atomizers. Initially a high approach-to-saturation temperature will be used, with additional tests at lower approaches, to determine the operating conditions before significant deposition occurs. The flow correction design will be similar to the schematic shown in Fig. 14. While this design may not achieve an acceptable flow distribution in the field pilot, the information obtained from these tests will help determine the appropriate modifications to correct the gas distribution.

E-SO_x FIELD TESTING AND DEMONSTRATION

HOST SITE

The host site for the E-SO_x field pilot demonstration is Ohio Edison's R. E. Burger Station located in Dilles Bottom, Ohio. The field pilot facility has been designed to use a slipstream of flue gas from either boiler unit 7 or 8. These are duplicate boilers constructed in the early 1950s. Both boilers are base loaded units. Each boiler has separate particulate control by ESPs manufactured by Environtech and installed in the early 1980s.

PILOT FACILITY

A simplified flow schematic of the 5 MWe E-SO_x pilot demonstration facility is shown in Fig. 15. A flue gas slipstream of approximately 400 m³/min (14,000 acfm) at 160°C (320°F) is taken from either boiler unit 7 or 8 and transported by an induced draft (ID) fan through the pilot facility ductwork. The flue gas takeoff is located just prior to the precipitator inlet ductwork. The pilot flue gas passes through an electrical resistance heater which controls the inlet flue gas temperature to the E-SO_x transition inlet. Venturi flow meters located in the inlet and outlet ductwork will be used to measure total flue gas flow entering and leaving the E-SO_x pilot facility.

At the inlet to the E-SO_x transition, a series of pneumatic atomizers introduce into the flue gas a fine mist of lime slurry. The lime slurry flow and composition is automatically controlled to maintain the desired stoichiometric ratio and flue gas outlet temperature. Hoppers located in the E-SO_x transition will collect solids. A series of gas flow straightening devices will be installed at the inlet to the ESP to ensure that the flue gas velocity distribution is acceptable. These devices which include the DID are also intended to reduce the amount of large, unevaporated lime slurry droplets that would otherwise enter the ESP. The flue gas then passes through the ESP where the particulate levels are reduced by precharger sections and four collection fields. An ID fan located just after the ESP transports the flue gas back to the appropriate boiler unit ductwork.

The relative locations of the major equipment are shown in the simplified plot plan view of Fig. 16. The E-SO_x field pilot has been equipped for slaking pebble lime and for storage and transport of lime slurry as well as process water to the atomizers. Waste ash product is removed from the hoppers with screw conveyors for off-site disposal. Two EPA supplied trailers will be used for onsite chemical analysis, process control, and data acquisition instrumentation. A flue gas sampling house is located between the inlet and outlet ductwork. The facility ductwork can be set to isolate the facility from the boiler ductwork and

allow it to be placed in recirculation mode. The recirculation mode will be used to maintain the facility at a sufficient temperature to prevent condensation, or to preheat the facility during cold start-up.

TEST PROGRAM

A test program has been established for the E-SO_x field pilot. The test program will include a 2 month period for construction checkout and shakedown testing of the facility. The simplified schedule of the test program is given in Fig. 17. Short term parametric (1 day), long term continuous operation (14 days), and operability (1 month) testing will be conducted during this test period. Analysis of performance data will be performed concurrently with the testing to ensure that test results are internally consistent and to determine when repeatability testing is required.

Test data will be collected with a computer-based automatic data acquisition system. The data will be reduced to characterize the E-SO_x system performance for both SO₂ and particulate removal at various operating conditions. The short term parametric tests will primarily focus on SO₂ reduction at various operating conditions. Due to the short duration of these parametric tests, the ESP will not have sufficient time to reach steady state operation. Therefore, detailed ESP testing will not be conducted. Long term operation and operability tests will be conducted at one set of conditions to characterize the ESP performance. In addition to the data automatically acquired, solid and liquid samples will be obtained as appropriate to determine the overall effectiveness of the E-SO_x process. Sampling ports located on the inlet and outlet ductwork will be used during long term and operability tests for particulate loading and resistivity, gas composition, and other measurements.

CONCLUDING REMARKS

The E-SO_x pilot demonstration program has been developed to obtain suitable design criteria for the E-SO_x technology and to demonstrate this technology at a 5 MWe pilot plant scale. By operating on a utility boiler flue gas slipstream at sufficient scale to produce meaningful data, the field test program will provide results representative of full scale operation. The results of these tests will provide an adequate design basis for scale-up to larger plant capacities.

ACKNOWLEDGMENTS

This field evaluation is being performed under a grant agreement (CDO/d-86-29) between the Ohio Department of Development's Coal Development Office and Babcock & Wilcox, with additional support from EPA's Air and Energy Engineering Research Laboratory. Southern Research Institute (SRI) is providing technical and economic analyses of ESP performance under E-SO_x conditions through a cooperative agreement with EPA. The Ohio Edison Company is providing site and utilities for the field demonstration at its R. E. Burger Plant.

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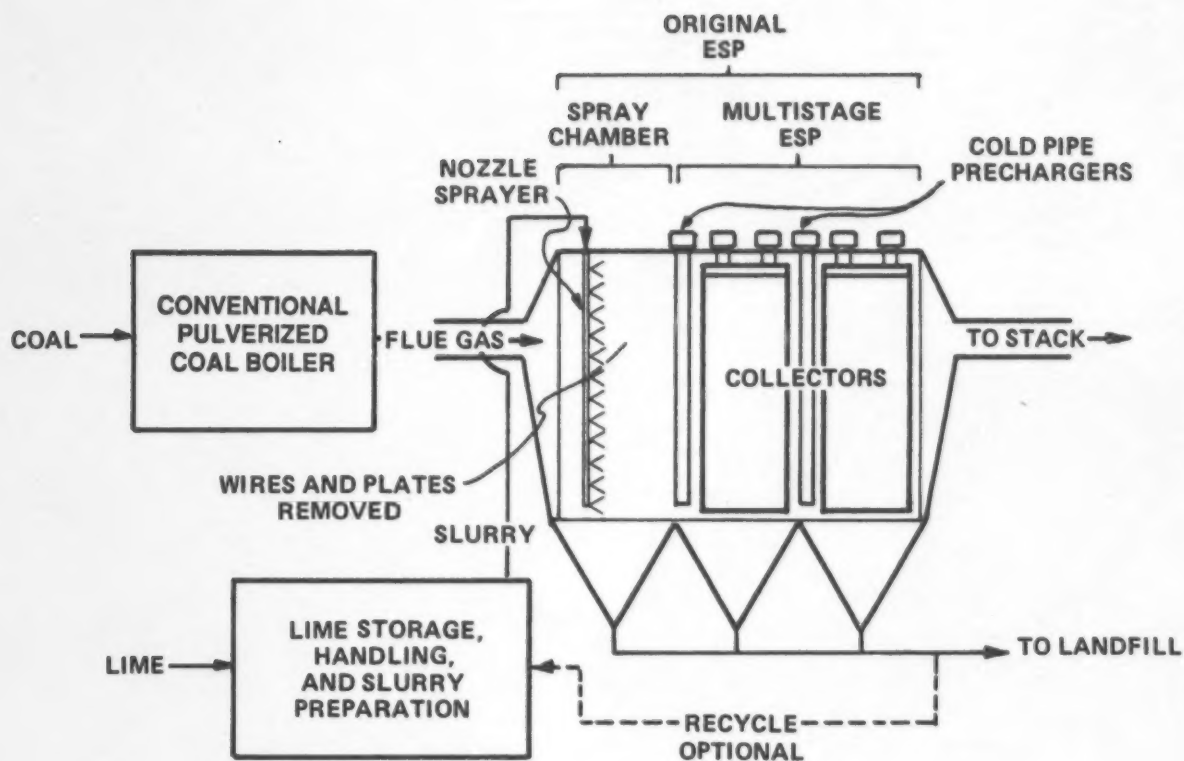


FIGURE 1 SCHEMATIC OF E-SO_x PROCESS

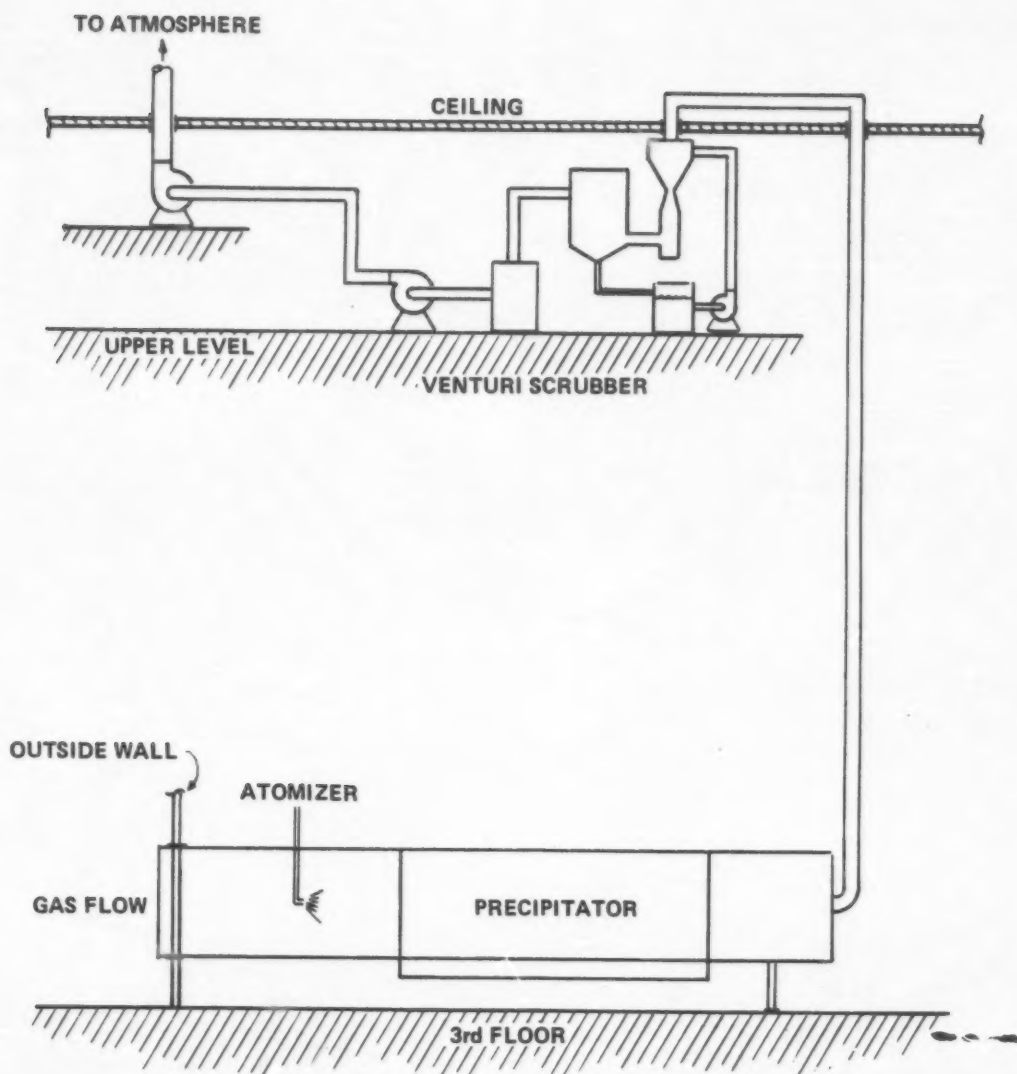
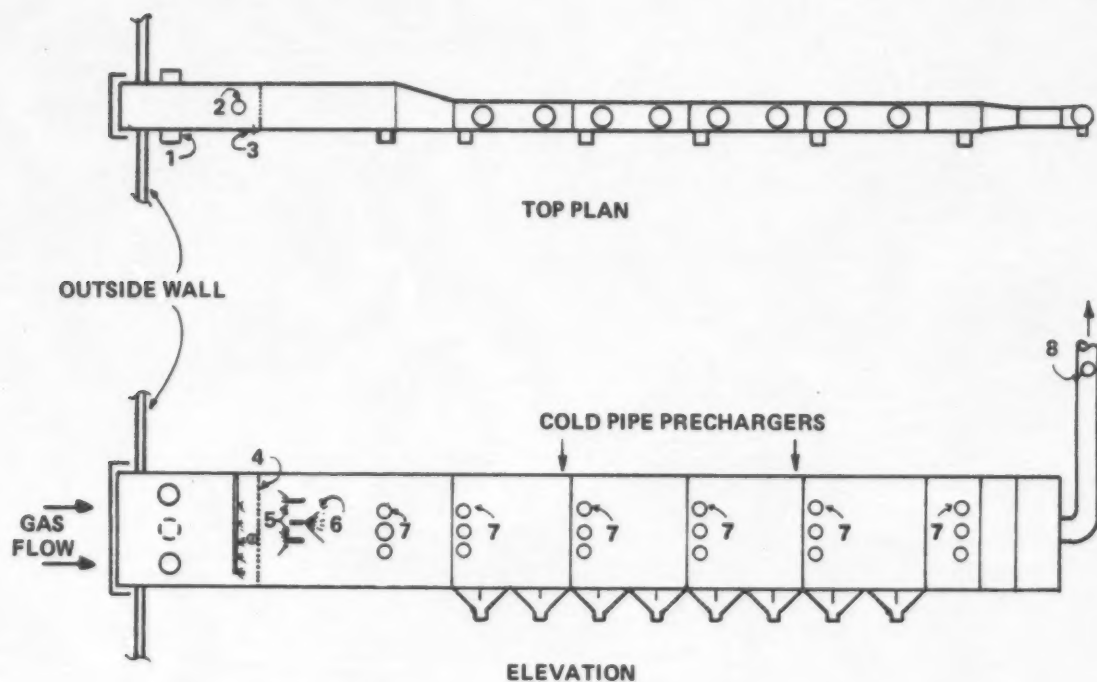


FIGURE 2 EPA E-SO_x PILOT FACILITY SCHEMATIC



1. NATURAL GAS BURNERS
2. SO₂ INJECTORS
3. BURNER TEMP. CONT. T. C. S
4. PERFORATED PLATE
5. ASH INJECTORS (AGAINST GAS FLOW)
6. ATOMIZER TIP
7. SAMPLING PORTS
8. OUTLET SAMPLE TAP

**FIGURE 3 EPA E-SO_x PILOT FACILITY, 1000 acfm (28 m³/min)
ESP WITH SPRAY ZONE**

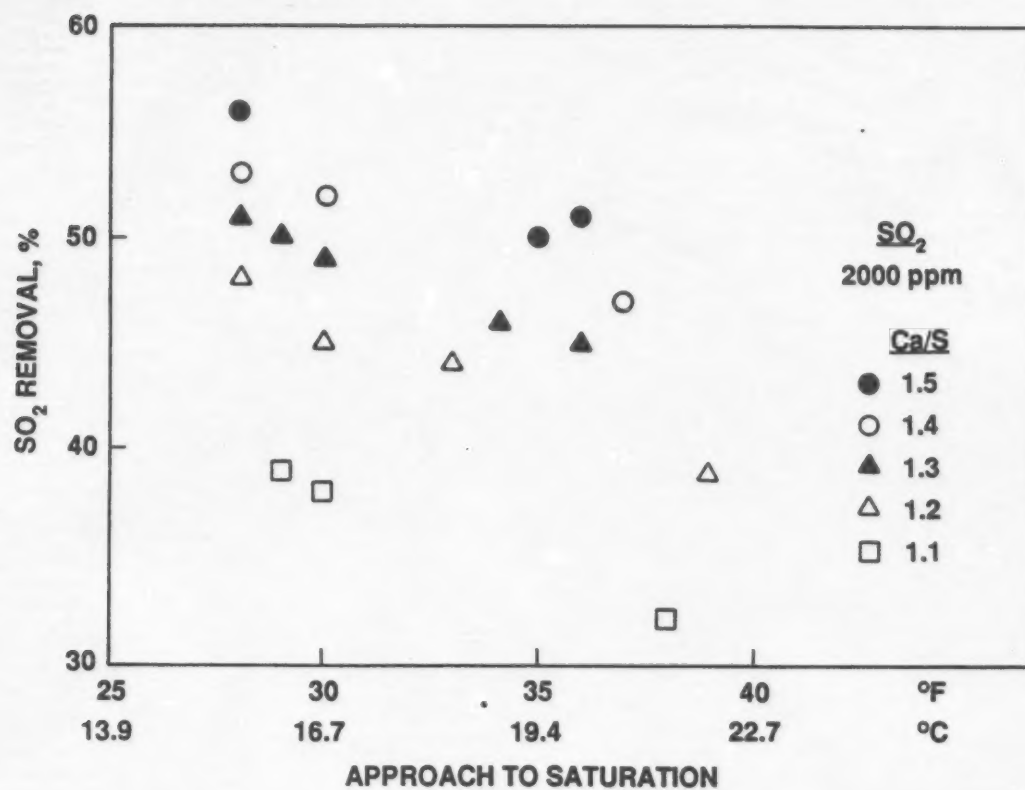


FIGURE 4 EFFECT OF APPROACH TEMPERATURE ON SO₂ REMOVAL AT SEVERAL STOICHIOMETRIC RATIOS

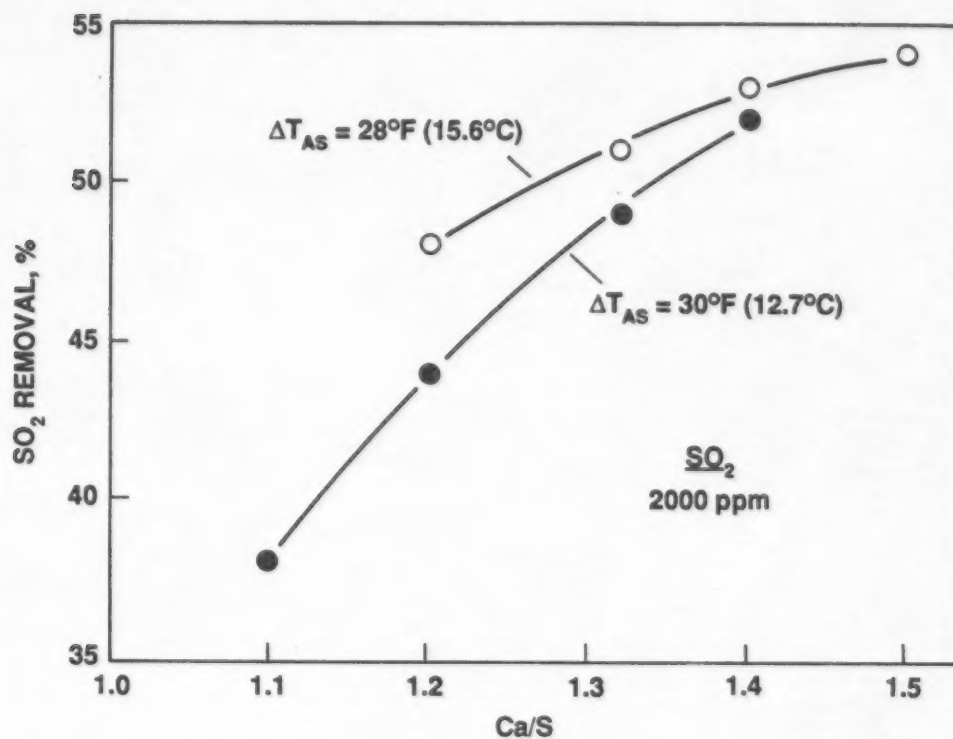


FIGURE 5 EFFECT OF STOICHIOMETRIC RATIO ON SO₂ REMOVAL AT TWO APPROACHES TO SATURATION

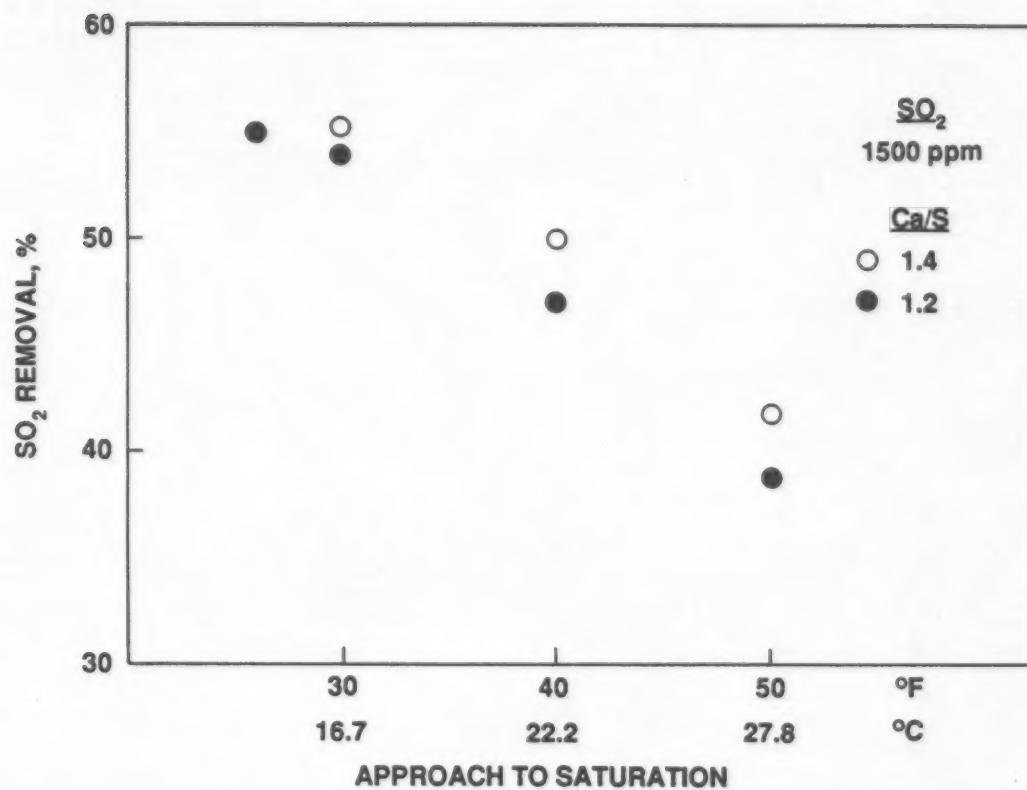


FIGURE 6 EFFECT OF APPROACH TEMPERATURE ON SO₂ REMOVAL AT TWO STOICHIOMETRIC RATIOS

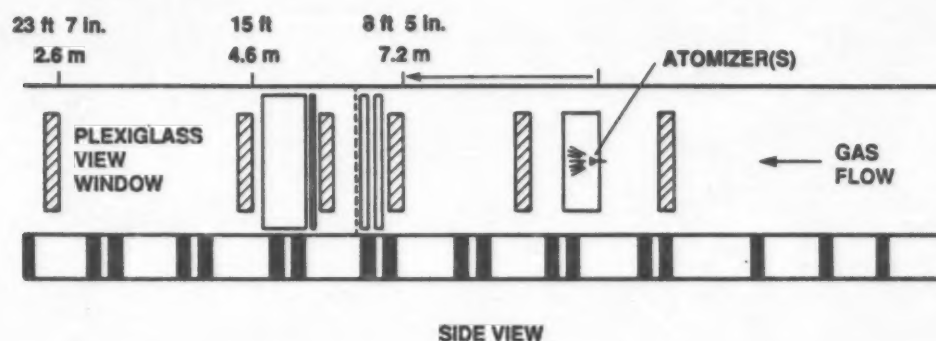
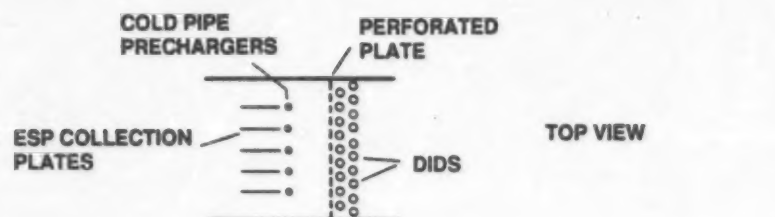


FIGURE 7 SCHEMATIC OF TEST FACILITY AND DID

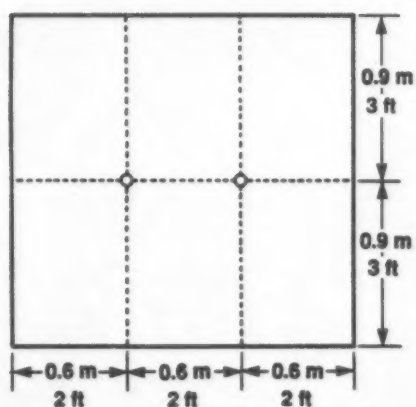


FIGURE 8 2 x 1 ATOMIZER
ARRAY SPRAY

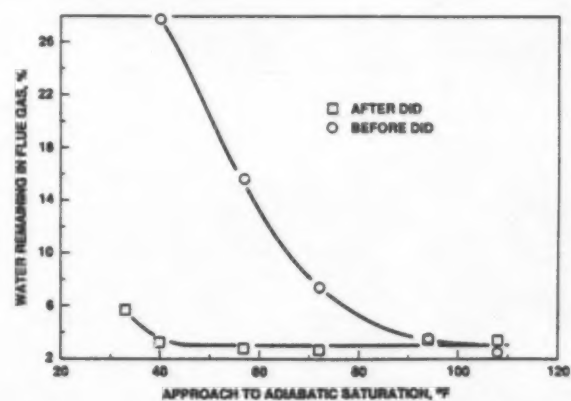


FIGURE 9 DID REMOVAL EFFICIENCY (DID - 50%
OPEN AREA; 2.8 m (9.2 ft) DOWNSTREAM
OF ATOMIZERS)

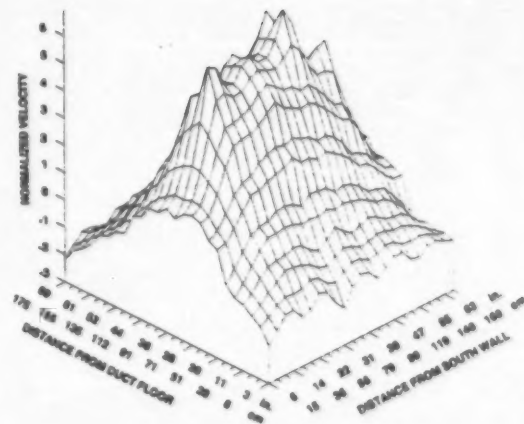
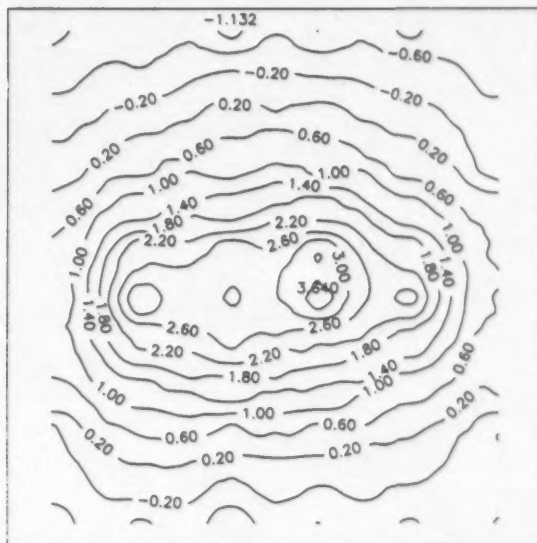


**FIGURE 10 VELOCITY CONTOUR PLOTS AT DID INLET
DID 2.8 m (9.2 ft) DOWNSTREAM OF ATOMIZERS**

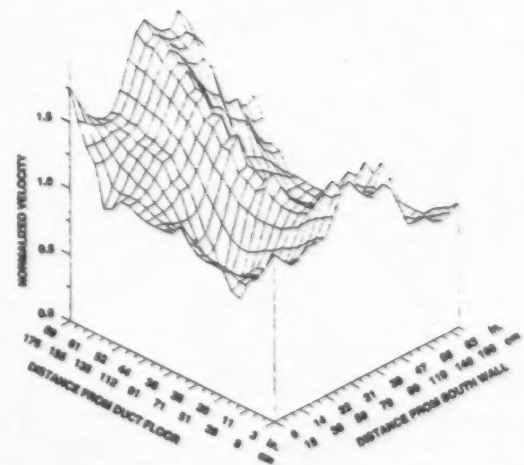
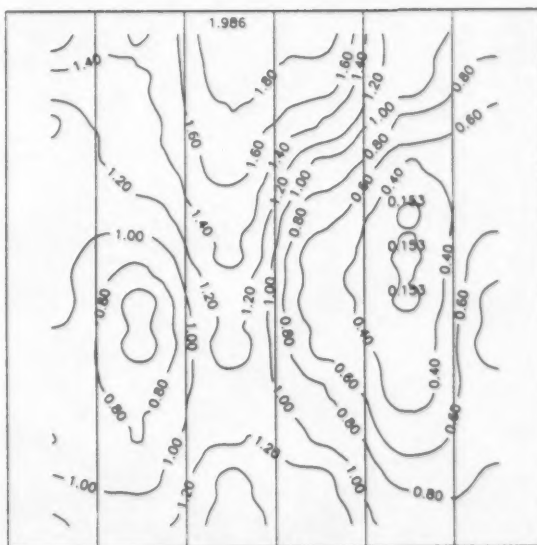


**FIGURE 11 VELOCITY CONTOUR PLOTS AT DID OUTLET
DID 2.8 m (9.2 ft) DOWNSTREAM OF ATOMIZERS**

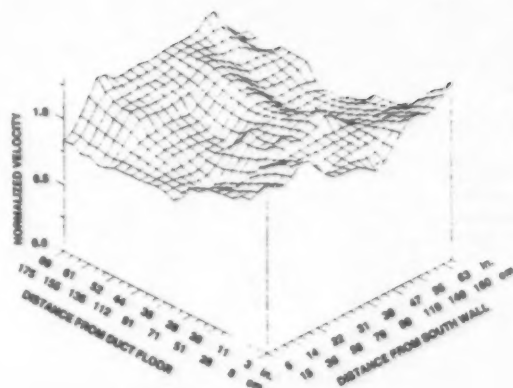
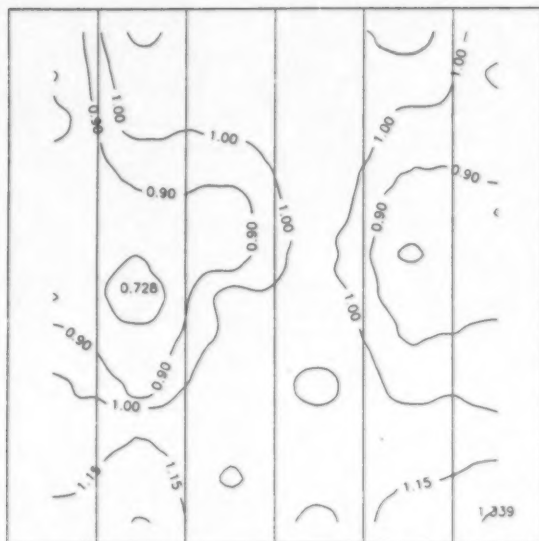


FIGURE 12 VELOCITY CONTOUR PLOTS AT DID OUTLET THAT ACHIEVED THE IGC1 CRITERIA DID 2.8 m (9.2 ft) DOWNSTREAM OF ATOMIZERS

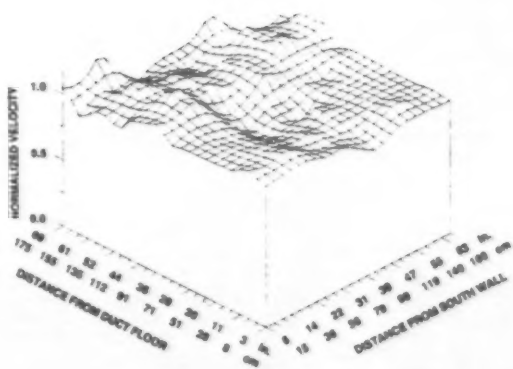
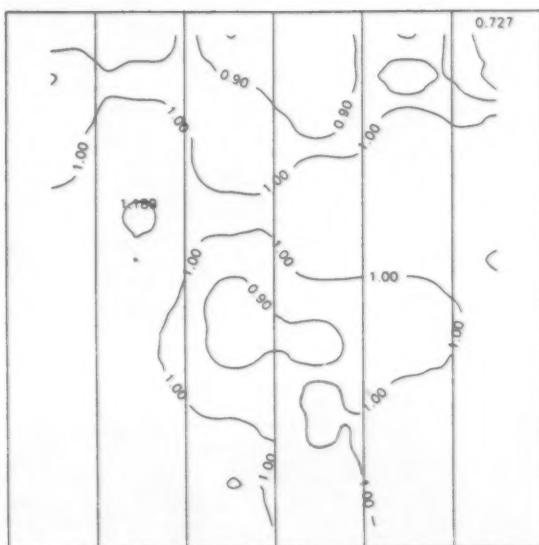


FIGURE 13 VELOCITY CONTOUR PLOTS AT DID OUTLET THAT ACHIEVED THE IGC1 CRITERIA DID 4.75 m (15.6 ft) DOWNSTREAM OF ATOMIZERS

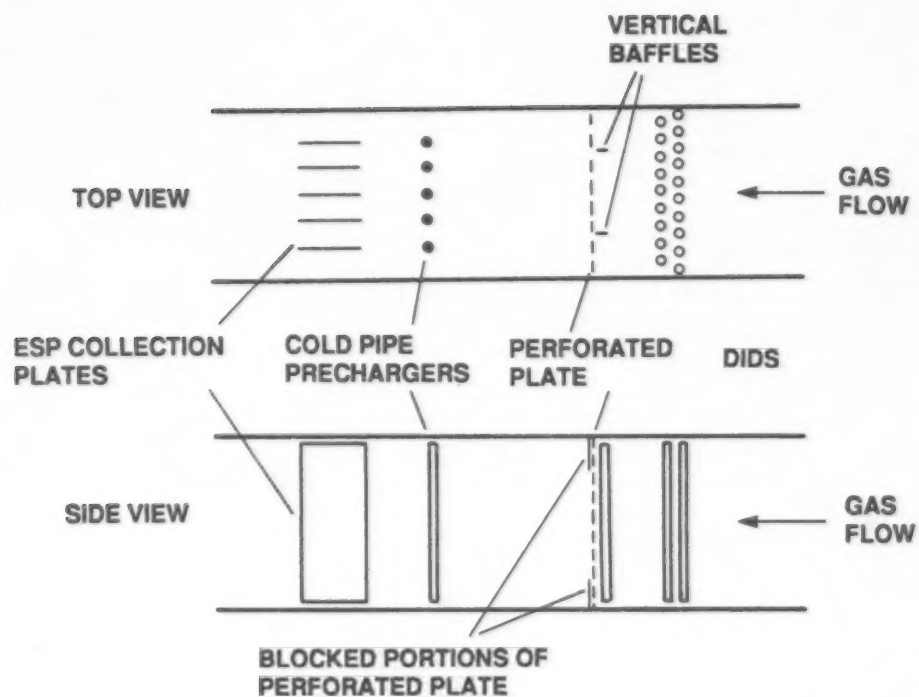


FIGURE 14 SCHEMATIC OF FLOW CORRECTION DEVICES WHICH SATISFIED THE IGC/ STANDARDS AT DID 2.8 m (9.2 ft) DOWNSTREAM OF ATOMIZERS

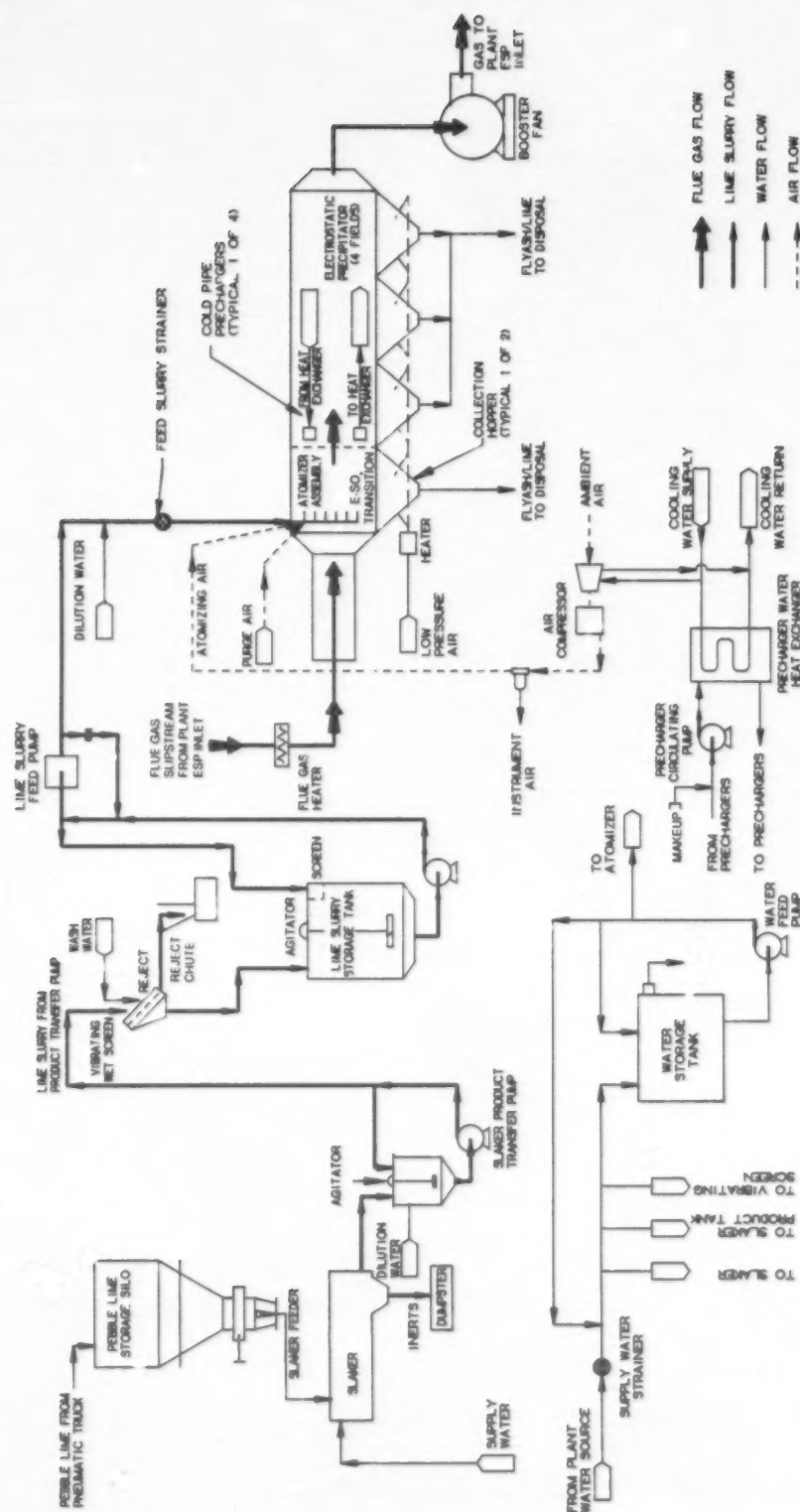
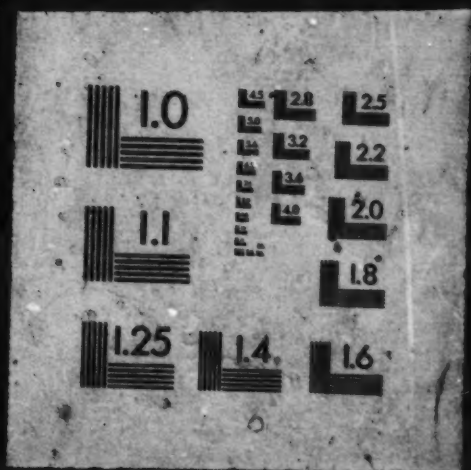


FIGURE 15 QUALITATIVE FLOW DIAGRAM FOR THE E-SO_x FIELD DEMONSTRATION PILOT PLANT

60F7

PB 89

172 175



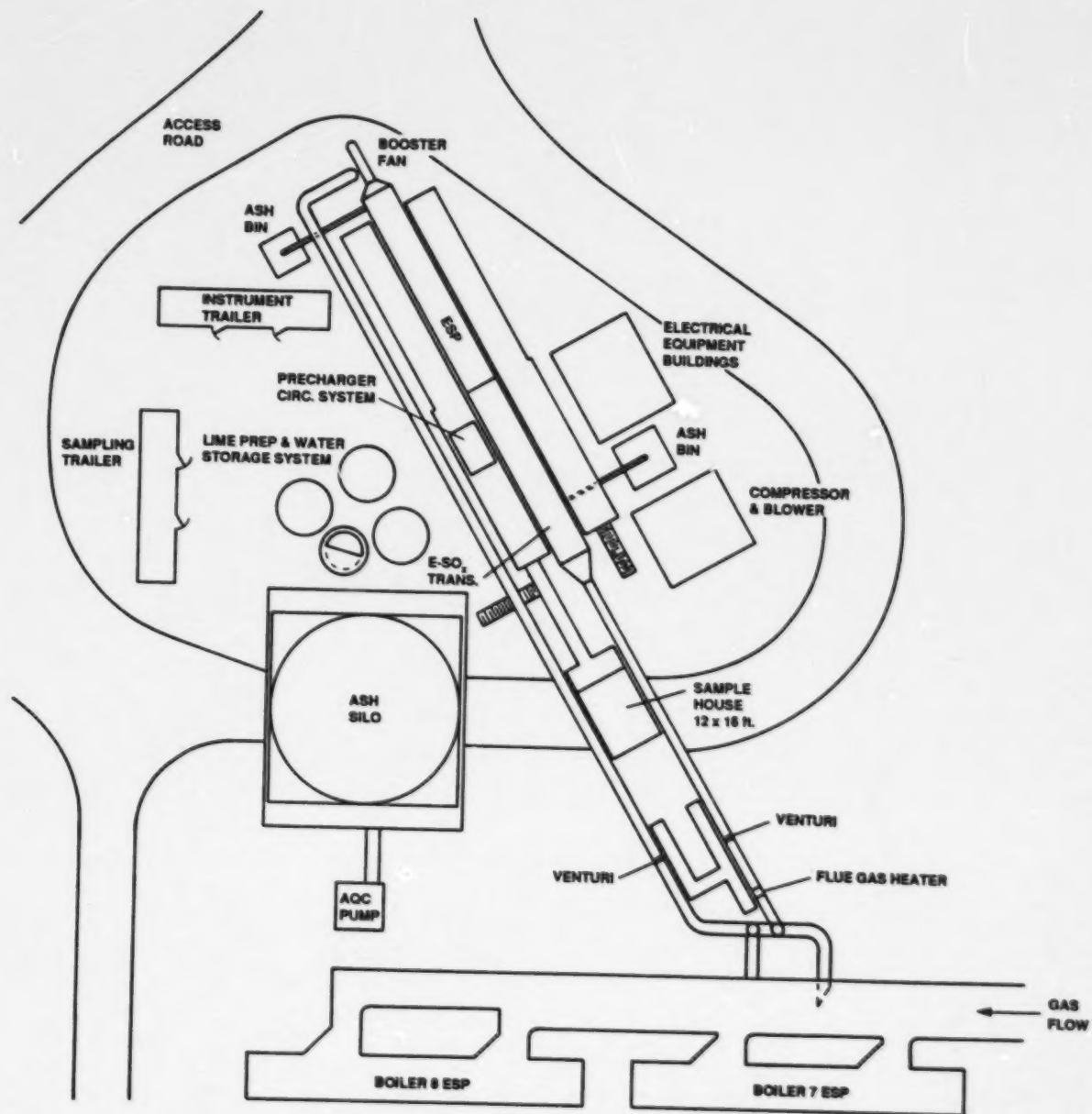


FIGURE 16 E-SO₂ GENERAL ARRANGEMENT
SITE PLAN

E-SO _x FIELD PILOT OPERATION	MONTH													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CONSTRUCTION CHECKOUT	■	■												
SHAKEDOWN TESTING		■	■	■										
CONFIGURATION TESTING				■	■	■								
BASELINE ESP TESTS				■	■									
ATOMIZER LOCATION				■	■									
FLUE GAS TEMPERATURE					■									
TEST PLAN UPDATE					■									
PARAMETRIC TESTING					■	■	■	■	■	■				
TEST SERIES 1 - SO ₂					■	■								
TEST SERIES 2 - SO ₂						■	■							
SRI ESP TEST 1							■							
INTERIM RESULTS MTG							■							
TEST SERIES 3 - SO ₂								■	■					
TEST SERIES 4 - SO ₂									■	■				
SRI ESP TEST 2									■					
INTERIM RESULTS MTG										■				
FOLLOW-UP TESTS										■	■			
OPERABILITY TESTING											■	■	■	
PRIMARY TEST											■	■		
ESP TESTING												■		
ALTERNATE CONDITIONS												■	■	
FIELD TEST REPORT													■	■

FIGURE 17 E-SO_x FIELD PILOT TEST PROGRAM SCHEDULE

TABLE 1. COMPARISON OF SO₂ REMOVAL BY SLAKED AND HYDRATED LIME
AT 2100 ppm SO₂

Lime	Approach to saturation* (°F)	Calcium-to-sulfur ratio	SO ₂ removal (%)
Hydrate	34	1.5	46
Slaked	36	1.5	54
Hydrate	38	1.1	32
Slaked	38	1.1	38
Hydrate	40	1.5	43
Slaked	40	1.2	43

* °C = °F/1.8

TABLE 2. E-SO_x FIXED CONDITIONS FOR SO₂ REMOVAL STUDIES

Air flow	28 m ³ /min (1000 acfm)
Inlet temperature	149°C (300°F)
SO ₂ concentration	2000 ppm
Fly ash concentration	1.9 g/l (1 gr/ft ³)
Nozzle configuration	Single two-fluid Casterjet oval spray pattern
Inlet chamber	1.5 m (5 ft) spray chamber plus 1.2 m (4 ft) ESP section

TABLE 3. EFFECT OF FLY ASH ON SO₂ REMOVAL AT
2000 ppm SO₂

ΔT_{AS}^* (°F)	Ca/S	Fly ash ⁺ (gr/ft ³)	SO ₂ removal (%)
28	1.4	0	49
28	1.3	1.0	50
35	1.5	1.0	50
35	1.5	0.25	52
36	1.5	0	52
37	1.3	0	45
37	1.4	1.0	47

* °C = °F/1.8

+ g/m³ = gr/ft³ x 2.3

TABLE 4. E-SO_x PARTICULATE REMOVAL EFFICIENCIES FOR VARIOUS ESP
ELECTRICAL CONFIGURATIONS

Sections energized 38 kV	Cold pipe 38 kV	Approach temperature* (°F)	Particulate	ESP efficiency (%)	Emission rate ⁺ lb/10 ⁶ Btu
2, 3, 4	Yes	30	E-SO _x & fly ash	99.5	0.017
2, 3, 4	No	30	Fly ash	97.9	0.032
2, 3, 4	No	30	E-SO _x & fly ash	98.5	0.030
2, 3	No	30	E-SO _x & fly ash	98.6	0.088
2, 3	No	35	Fly ash	95.6	0.058
2, 3, 4	No	100	Fly ash	97.6	0.030
2, 3, 4	Yes	100	Fly ash	97.8	0.038
2, 3, 4	Yes	160 [#]	Fly ash	89.0	0.128

* °C = °F/1.8

+ ng/J = lb/10⁶ Btu x 430.5

No moisture injection

UNPRESENTED PAPERS

THE ECOTECH DRY SCRUBBER—
FOR THE SIMULTANEOUS DRY SCRUBBING OF HIGH TEMPERATURE
HARD PARTICULATE MATTER, CONDENSABLE SOLIDS,
AND NOXIOUS GASES ENTRAINED IN A GAS STREAM

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ABSTRACT

The ECOTECH Dry Scrubber System (EDSS), is an effective device at high temperatures, for the collection of fine particulate matter, condensable solids and noxious gases. This is accomplished by means of "ADSORPTION" and "ABSORPTION", with an ionized sorbent material. This material is then removed from the gas stream by larger media particles, which are then screened of reaction product and recycled for reuse.

The system has been tested on the following effluent:

- 1 Hot Mix Asphalt
- 2 Calcining Rotary Kiln
- 3 Coal Fired Boiler
- 4 Waste Incineration
- 5 Copper Production — Reverberatory Furnace
- 6 Magnetohydrodynamic Test Facility
- 7 Copper Production — 10 MW Electric Arc Furnace
- 8 Steel Production — Open Hearth Furnace
- 9 Precious Metals Recovery — Volatilization Chloridizing Roast

INTRODUCTION

The simultaneous DRY scrubbing of hard particulate matter, condensable solids, SO_2 , as well as other acid gases entrained in a gas stream, has been a major problem to industry for a number of years. A considerable amount of research has been conducted using baghouse and Electrostatic Precipitation

technology in conjunction with slurry and/or dry sorbent injection. In the case of a baghouse, this involves cooling the gas stream down to a temperature within the limits of the bag suppliers specifications. After cooling the gases, the operating temperature "window" narrows to within critical operating guidelines, in order to stay above the Acid Dew Point (see figure 1). The purpose of this paper is to present a technology that utilizes the technologies mentioned above without the inherent problems associated with a baghouse or electrostatic precipitator.

ECOTECH DRY SCRUBBER DESCRIPTION

The ECOTECH dry scrubber consists of a charged dry sorbent injection system used in conjunction with a gravel bed filter system. The sorbent injection system is located upstream of the gravel bed filter.

The distance from the gravel bed filter is determined by the average operating temperature of the gas stream. The sorbent material is entrained in a high velocity ambient air stream and passed through a high voltage charging (ionizing) system, that places a static charge on the sorbent particles, prior to their entry into the hot gas stream.

The charged sorbent material is then intimately mixed and uniformly distributed in the hot gas, prior to its entry into the gravel bed filter. The inlet plenum to the gravel bed filter is sized to decrease the gas velocity and to act as a dropout chamber for the large particulate matter, that is formed by the agglomeration of sub-micron particulate matter and the charged sorbent material.

The gravel bed filter system consists of three 12 inch thick media beds (two moving and one static), placed four feet apart. Each moving bed consists of two perforated sheets of steel placed 12 inches apart. Each screen segment is filled with limestone rocks sized from $-3/4"$ to $1/4"+$, and is moved in a plug flow mode. The movement of the bed is dictated by the pressure drop across that bed. As the bed loads up with particulate matter and sorbent reaction products the pressure drop will increase and the photohelic® gauge will signal the bed to move downward. This will expose clean media to the dirty gases.

Any particulate matter passing through the first bed impacts with the second media bed. This media bed is also controlled with a photohelic® gauge that signals the bed to move when the pressure drop across the bed reaches a preset point (in inches of H_2O).

After passing through the second bed, all particulate and reaction product, (i.e., calcium sulfates and sulfites), have been removed from the gas stream. A third and final bed, using pumice as the media, removes any particulate reentrained by the movement of bed two. This third and final cleanup bed operates in a static configuration, and is purged by batching as the pressure drop across the bed requires.

The EDSS is shown schematically in Figure 2 and has a modular shape for easy access. Most of the operating parts are located outside of the gas stream, which allows easy access for maintenance.

The EDSS was tested on an extremely hot gas stream (operating at high temperatures eliminates the problems associated with the acid dew point). During normal operations all internal parts are coated with the sorbent material. If the temperature should drop below the acid dew point for a short period of time, the acids will preferably attack the sorbent material coating.

DRY CHARGED SORBENT INJECTION SYSTEM

Figure 3 is a flow schematic of the high voltage charged sorbent injection system. The sorbent material is introduced to a high velocity air stream by means of a venturi, and is then passed through a corona generated in the charging gun. This ionized sorbent material is then injected into the hot gas stream prior to its entry into the scrubber system. The charge placed on the sorbent particles causes the particulate matter in the gas stream to be "adsorbed". This in turn will form an agglomeration of the larger particulate matter, allowing for easy removal. The acids entrained in the hot gas stream will be absorbed by the sorbent material. A model of this process is shown below.

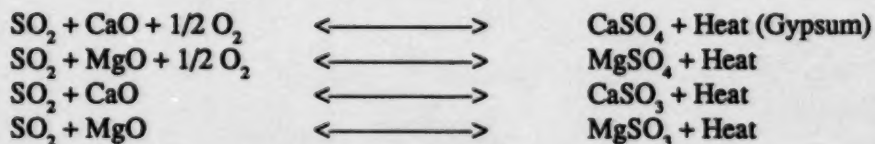
SORBENT/MEDIA REACTION PROCESS (1)

The Calcium Hydroxide was analyzed for the following:
(No Analysis was done on the TRONA)

1)	CaO	=	92.64%
2)	MgO	=	1.22%
3)	R ₂ O ₃	=	1.75%
4)	Insol Residue	=	2.86%
5)	SiO ₂	=	2.58%
6)	Loss of ignition	=	1.33%
7)	Undetermined	=	.20%
8)	Available CaO	=	90.10%
9)	Reactivity	=	HIGH

The R₂O₃ consists of the combined oxides (Iron, Aluminum, Phosphorus, Titanium and Manganese), as determined by ASTM C25 through 30. The Insol residue was determined by Perchloric Acid Method ASTM C25, Section 13 through 17. Loss of ignition includes free moisture, chemically combined "lattice" or "hydroxy" water, CO₂ and SO₂ as determined by ASTM C25, Sections 74 through 78.

The principal sorbent reactions are between the calcium/magnesium oxides in the sorbent and the sulfur oxides in the gas stream. The reaction products will be calcium sulfite, calcium sulfate (gypsum), magnesium sulfite, and magnesium sulfate. The reactions are shown below:



No reactions between the nitrogen or oxygen in the gas stream and the sorbent will occur.

Reactions between the other oxide species in the sorbent (i.e. iron, aluminum, phosphorus, titanium and manganese), and the sulfur oxides in the gas, are not considered significant. This is due to the low concentrations of these constituents in the sorbent.

Water vapor in the gas will not react with the sorbent at high temperature, but will react with the media as the temperature decreases toward the acid dew point.

The calcination reaction proceeds very slowly at temperatures below 1200°F. Above 1200°F the rate of reaction increases very rapidly up to 1650°F, where the partial pressure of CO_2 involved reaches 1 atmosphere. As a practical matter, the reactions between the limestone media and the sulfur oxides at temperatures in the range of 600-650°F is negligible. However, as the temperature approaches the acid dew point, the reaction will increase. The general concept of calcium/magnesium oxides reacting with sulfur oxides in the "dry" state is strongly influenced by temperature. Depending on temperature, one of two distinct mechanisms will occur. Below a given temperature, water vapor in the gas will form an adsorbate layer on the lime particle. Sulfur oxides will be absorbed into this layer where it will react (IN THE LIQUID PHASE), with the calcium oxide. Above a given temperature (IN THE GAS PHASE), sulfur oxides will react DIRECTLY with the solid calcium oxide. The rate of this reaction will increase as the gas temperature increases.

LABORATORY RESISTIVITY TESTS OF SORBENT SAMPLES (2)

Three samples of sorbent material were tested for electrical charge resistivity. The data was obtained according to the procedure outlined in IEEE Standard 548-1984 (descending temperature method only). The measured water vapor concentration (volume percent) is shown on the top of each plot. The calculated volume percent of water in ambient air was around 2%. However, the lowest water concentration that could be obtained by the equipment was 3.3%, so the second test had to be run at this humidity value. The sorbent was:

- | | | | |
|----|--|---|--------------------|
| a. | NaHCO_3 | — | Nacholite |
| b. | $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ | — | Diatomaceous Earth |
| c. | Ca(OH)_2 | — | Hydrated Lime |

Normally, it would be expected that a sample run in dry air would lie in a straight line. This is the case for the hydrated lime and diatomaceous earth samples. The NaHCO_3 seems straight in the high temperature limit, but curves as the temperature decreases. This is probably due to the error in measuring very high resistivity (alternatively, very small measured currents), as well as the possibility that alternative paths of lower resistivity (than those through the sample), might exist (i.e., a leakage current). The hydrated lime sample had such low resistivity for temperatures greater than roughly 230°C, that current limits for the equipment were exceeded. Thus, no data for this sample was obtainable in the high temperature limit. See FIGURE 3 and FIGURE 4.

The data obtained with water vapor present were typical in character; a region where volume conduction through the sample was dominant (temperatures greater than about 150°C), a region where conduction along the surface of particles was dominant (temperatures less than about 110°C), and a transition area (the Peak) where volume and surface conduction are equally important. The dip in the high

temperature data of the NaHCO_3 is probably an experimental error, because it was expected that this line would lie along a straight line. Again, the high temperature limit for the hydrated lime was unattainable due to current equipment limitations.

RESULTS OF RESISTIVITY TESTS

As indicated in the above report, the resistivity at moment of charge starts declining as the temperature of the gas stream increases. The temperature of the sorbent transport air, at time of injection, is around 190°F.

The following sections give the test conditions, procedures, filter efficiency, sorbent injection rates, SO_2 levels, particulate removal efficiencies, and bed pressure drop.

Test Conditions

The EDSS was installed to accept the simulated industrial effluent generated from a Magnetohydrodynamic Test Stand (MHD) (3). The fuel feed to the MHD was modified to accommodate mixtures of particulate matter and elemental sulfur. The particulate matter used was fly ash from a power utility, and salt cake from a paper mill. The SO_2 was generated by mixing elemental sulfur with the fuel prior to burning.

Test Procedures

An independent test laboratory (4) was contracted to conduct simultaneous sampling from the inlet and outlet of the EDSS, using EPA approved methods (5). Specifically, Method 1 was used to determine the number of sample points; Method 3 to determine the molecular weight of the stack gas; and Methods 5 and 6 were used to determine flow rates, moisture content, particulate matter and SO_2 emissions. The sampling train used was identical to that described in Method 5, except that the contents of the impingers were modified by replacing the water with 6% peroxide for capturing the sulfur dioxide.

Filter Efficiency, Sorbent Injection Rates

The unit showed very good efficiencies in particulate and SO_2 removal when using Calcium Hydroxide as the sorbent material. The SO_2 efficiencies reached were enhanced by the use of trona as the sorbent material. The sorbent injection rate was determined by the stoichiometric ratio of the sorbent, and the sulfur content of the gas stream. The sulfur content of the gas stream was determined by the amount of elemental sulfur mixed with the fuel going into the MHD combustor. The combustor was achieving a 99.4% conversion from elemental sulfur to SO_2 , at an average injection rate of 7 lbs. per hour. A series of tests were conducted utilizing trona as the sorbent material. The stoichiometric ratio of the trona was 1.5 : 1.

Continuous Monitoring For SO₂

Mississippi State University supplied a Thermoelectron Sulfur Dioxide gas monitor to measure SO₂ at three different locations in the scrubber system. The sample lines were heated to 325°F in order to stay above the acid dew point, and the probes had glass filters to remove particulate matter prior to entry into the sample line. The EDSS was modified to have seven sample points (see FIGURE 7). The SO₂ efficiencies were tested at points #1, #4 and #7. Sample point #7 was located after the gases had passed through the EDSS, which gave the overall efficiency of the system. Sample point #1 was located before the sorbent injection system, which allowed for the measurement of incoming SO₂ in parts per million (ppm). Sample point #4 was located four feet after the sorbent injection point, and measured SO₂ removal by the sorbent prior to its entry into the scrubber. The following is a breakdown of the sampling at different sample points. The sorbent used was Trona.

SAMPLES WITH NO SORBENT INJECTION:

Inlet SO ₂ ppm	Outlet SO ₂ ppm	Percent Reduction
1050	900	14%
1050	850	19%
1300	1000	23%
1400	1000	29%
1500	1000	33%

NOTE: Sample point locations #1 and #7 (figure 7).

SAMPLES WITH TRONA INJECTION:

Inlet SO ₂ ppm	Outlet SO ₂ ppm	Percent Reduction
1500	600	60%
1700	500	71%
1800	450	75%
1800	500	71%
1700	400	76%
1800	400	78%
1800	400	78%
1850	400	78%

NOTE: Sample point locations #1 and #7 (figure 7). Stoichiometry of 1.5.

SAMPLE WITH TRONA INJECTION

Inlet SO ₂ ppm	Outlet SO ₂ ppm	Percent Reduction
800	400	50%
800	400	50%
800	400	50%
800	350	56%

NOTE: Sample point locations #4 and #7 (figure 7). Stoichiometry of 1.5.

The data above indicates a 50% reduction of SO₂ at the point of sorbent injection, and 25% reduction with the gravel bed filter, for an overall average total efficiency of 75%. These efficiencies were reached without water (as is done in slurry injection), with a maximum pressure drop of 11" H₂O.

Particulate Matter Removal Efficiencies

The following is a breakdown of the particulate removal efficiencies achieved. The particulate matter was a mixture of fly ash and salt cake. The inlet grain loadings do not include the amount of sorbent material injected. If they did, this would add approximately 4 gr./dscf to the inlet loading.

Inlet gr./dscf	Outlet gr./dscf	Percent Reduction
3.09	.03	99%
.38	.09	77%
1.11	.03	97%
1.18	.009	99%
1.85	.02	99%
4.16	.02	99%
.90	.02	97%
1.72	.02	99%
1.31	.02	98%
3.16	.03	99%
3.59	.04	99%
4.33	.03	99%
2.44	.03	98%
1.94	.02	98%
1.88	.02	99%

NOTE: This represents an average inlet loading of 2.20 gr./dscf, and an average outlet loading of .03 gr./dscf, for an average efficiency of 98.6%. If you were to correct for the sorbent injection, the efficiency would increase to 99.51%.

Bed Pressure Drop

The pressure drop across each individual bed is controlled by the amount of grain loading encountered by that bed. As the grain loading on the bed increases, the pressure drop will increase, and a Photohelic® gauge will signal the bed to move downward in order to expose clean media to the gases. This process will continue until the pressure drop decreases to a preset range. Media bed one and two operate under this configuration. When the pressure drop across bed three reaches a preset point, the bed is completely emptied and then refilled with clean media or "purged". FIGURE 6 shows the pressure drop encountered for the complete test period. The pressure drop can be projected by the following widely accepted mathematical model (4):

$$\Delta p = \frac{fz u_G^2 (1-\epsilon)^3 \rho_G}{d_c \epsilon^3}$$

$$f = \frac{150}{N_{Re}} + 1.75$$

$$N_{Re} = \frac{d_c u_G \rho_G}{\mu_G (1-\epsilon)}$$

Where:

- Z = Bed Depth (30.42cm)
- d_c = Granule Diameter (10 to 14 Mesh Avg. 2.4mm)
- u_G = Gas Viscosity, Air (.018 Centpoise, Std.)
- N = Number of impaction Stages (1)
- ε = Bed Porosity, Fraction (.43 ± .02)
- R_e = Renolds Number (.0084)
- f = Friction Factor (.048)
- ρ_G = Gas Density (q/cm³ air . .002)

In accordance with this calculation the Δp on a three bed system will be between -4.86" and -6.84" H₂O. This theoretical model supports our actual experience with operating pressure drops. Many hours of operation during pilot studies have shown that the optimum Δp range is between 6" to 7" H₂O.

SUMMARY

The EDSS is a totally dry scrubber that has been tested on numerous industrial gas streams. This system consistently shows high efficiencies in the removal of Hard Particulate matter, condensible solids and noxious gases. This is accomplished by a patented ionizing dry sorbent injection system, (that ionizes the sorbent material prior to its entry into the gas stream), used in conjunction with a series of gravel bed filters that are moving downward (in a plug flow mode), as the pressure drop across that bed requires.

During the sorbent injection phase, three reactions take place that enhance the ability of the scrubber.

- 1) Sorbent Material — The selection of the sorbent is determined by which dry chemical will readily react with the gaseous pollutants entrained in the gas stream, and the highest operating temperature the source process will allow.
- 2) Adsorption — After the sorbent material has passed through the corona discharge (created in the high voltage system), and injected into the process gas stream, the sub-micronic particulate matter will be attracted to the sorbent particles, and will form an agglomeration of the particles for easy removal.
- 3) Absorption — As the temperature of the gases drop near the acid dew point, the condensible solids will react with the sorbent material.

The gravel bed filter (used in conjunction with the patented sorbent injection system), serves a number of functions in the scrubbing of the sorbent material and particulate matter entrained in the process gas stream.

- 1) Diffusion, Inertia, and Impaction — As the pollutants enter the inlet plenum to the scrubber, the velocity is reduced to allow for the natural dropout of the heavy particulate matter. This particulate matter then collides with the media particles in the first bed. Due to the inertial and impaction forces, the particulate and sorbent are carried out of the bed and screened off for disposal. The media is then returned to the unit for reuse.
- 2) Heat Exchanger — After the hot process gases have passed through the first bed, a considerable amount of the heat has been transferred to the media particles. Upon entry into the second media bed, the gases are nearing the acid dew point, where an absorbate layer is formed on the media particles. This layer is removed through screening and the media particles are returned to the unit for reuse.

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4. D. Russel of Environmental Monitoring Laboratories, for collecting the samples and the laboratory analytical work.
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Baghouse Operating Window

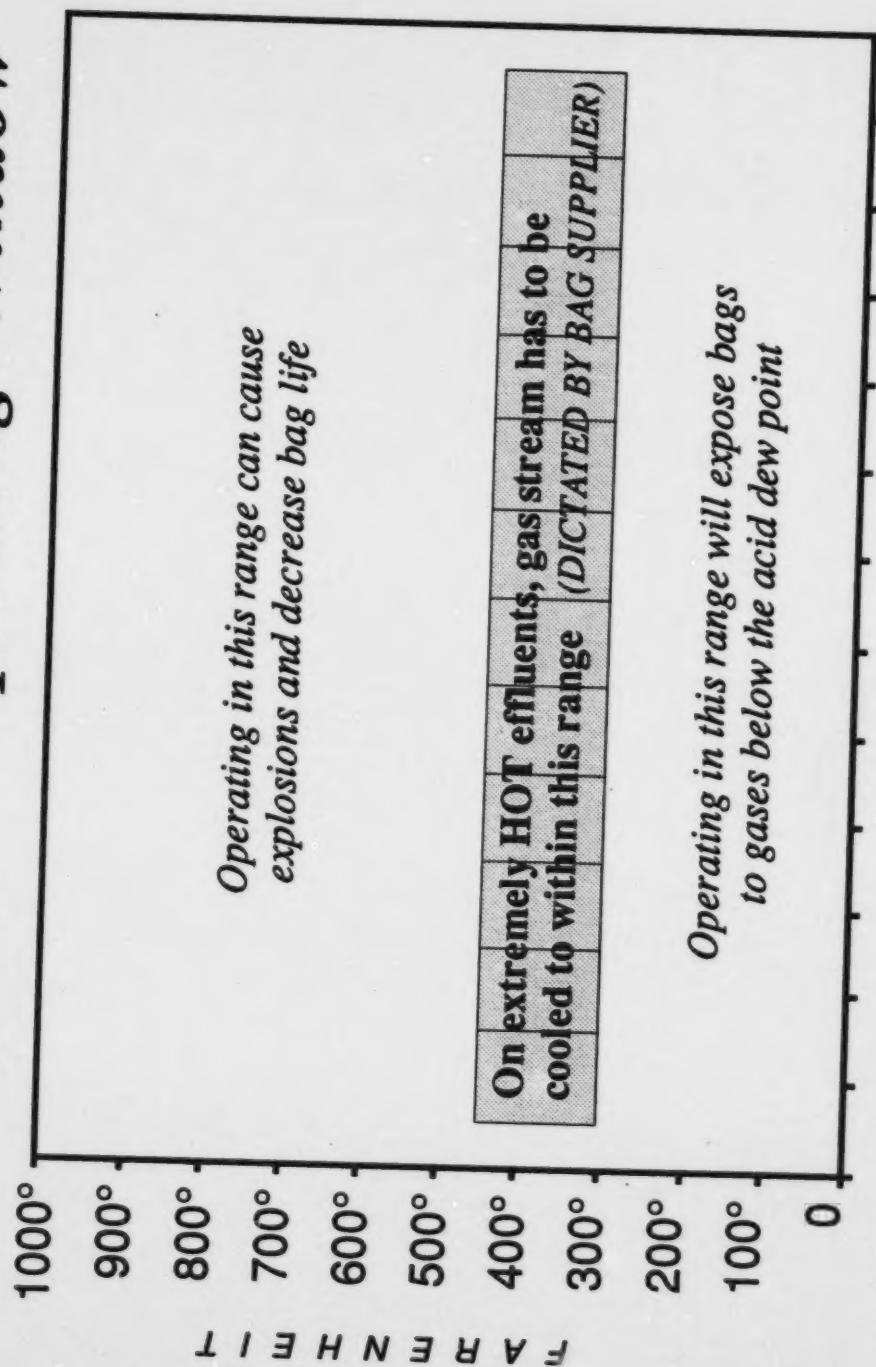
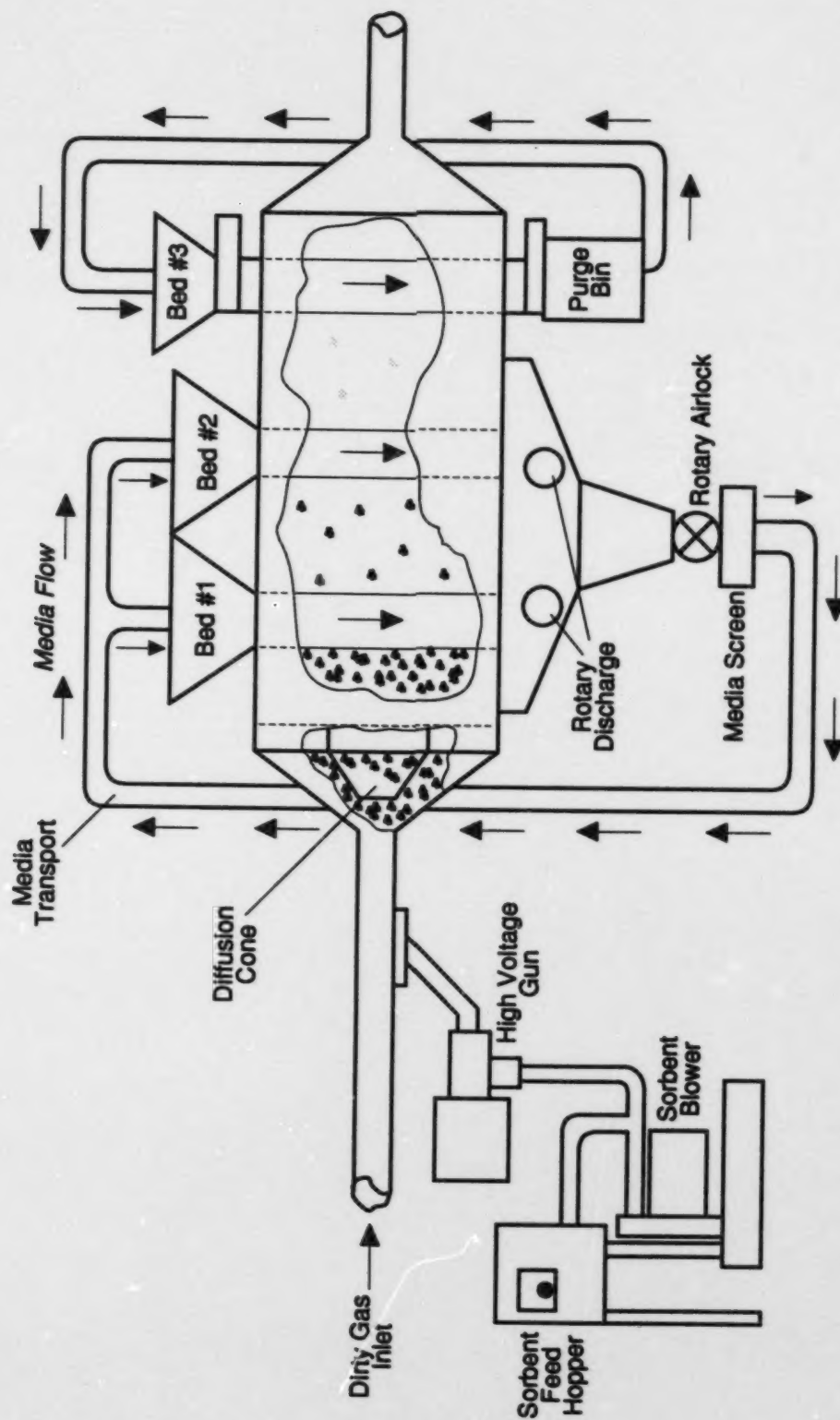
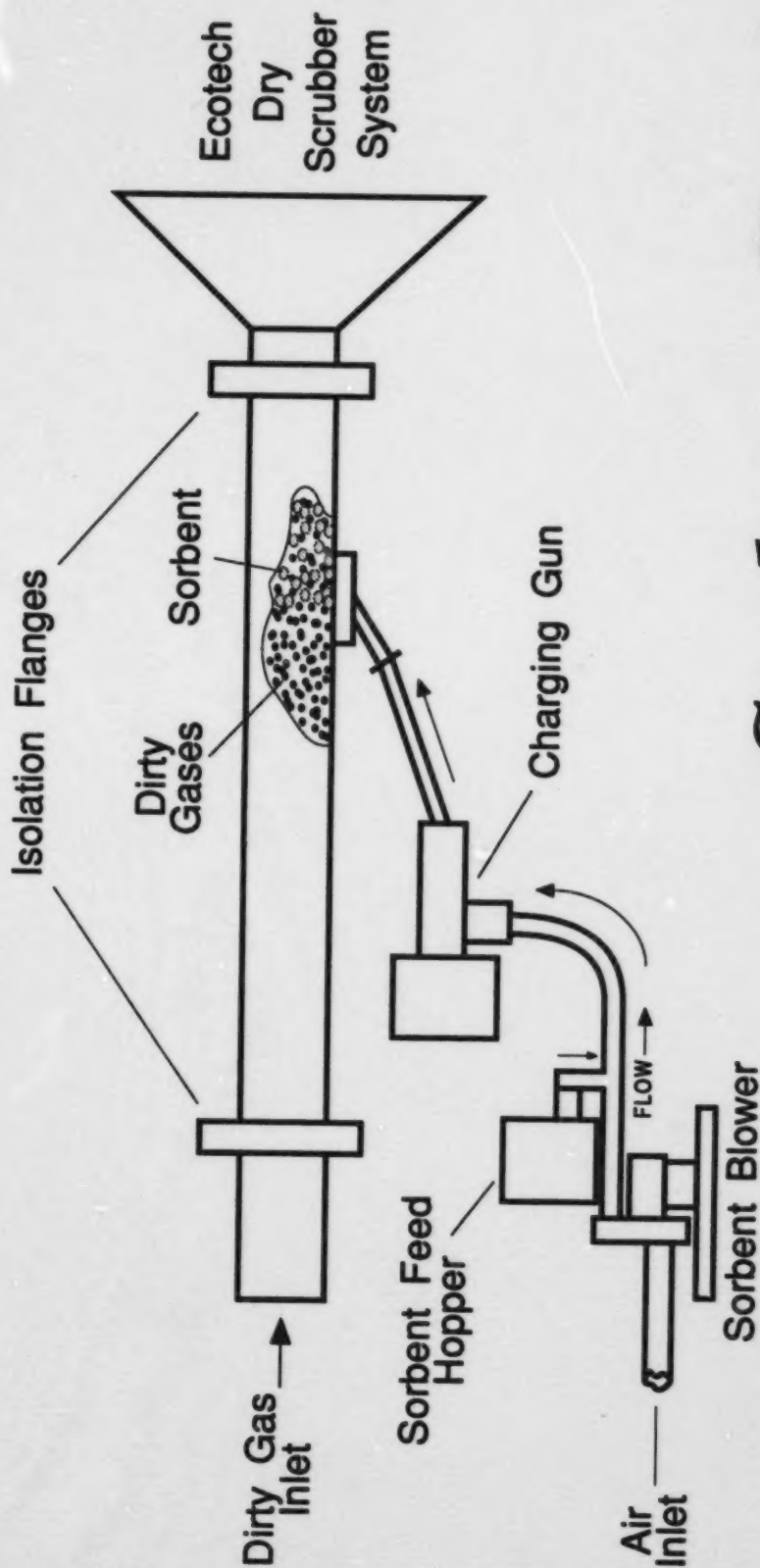


FIGURE 1



EDSS Flow Schematic

FIGURE 2



Sorbent Feed Schematic

FIGURE 3

PROJECT: 5901
DATE: 9/4/85
% H₂O: 0.00

○ HYDRATED LIME
□ DIATOMACEOUS EARTH
◇ NaHCO₃ SORBENT

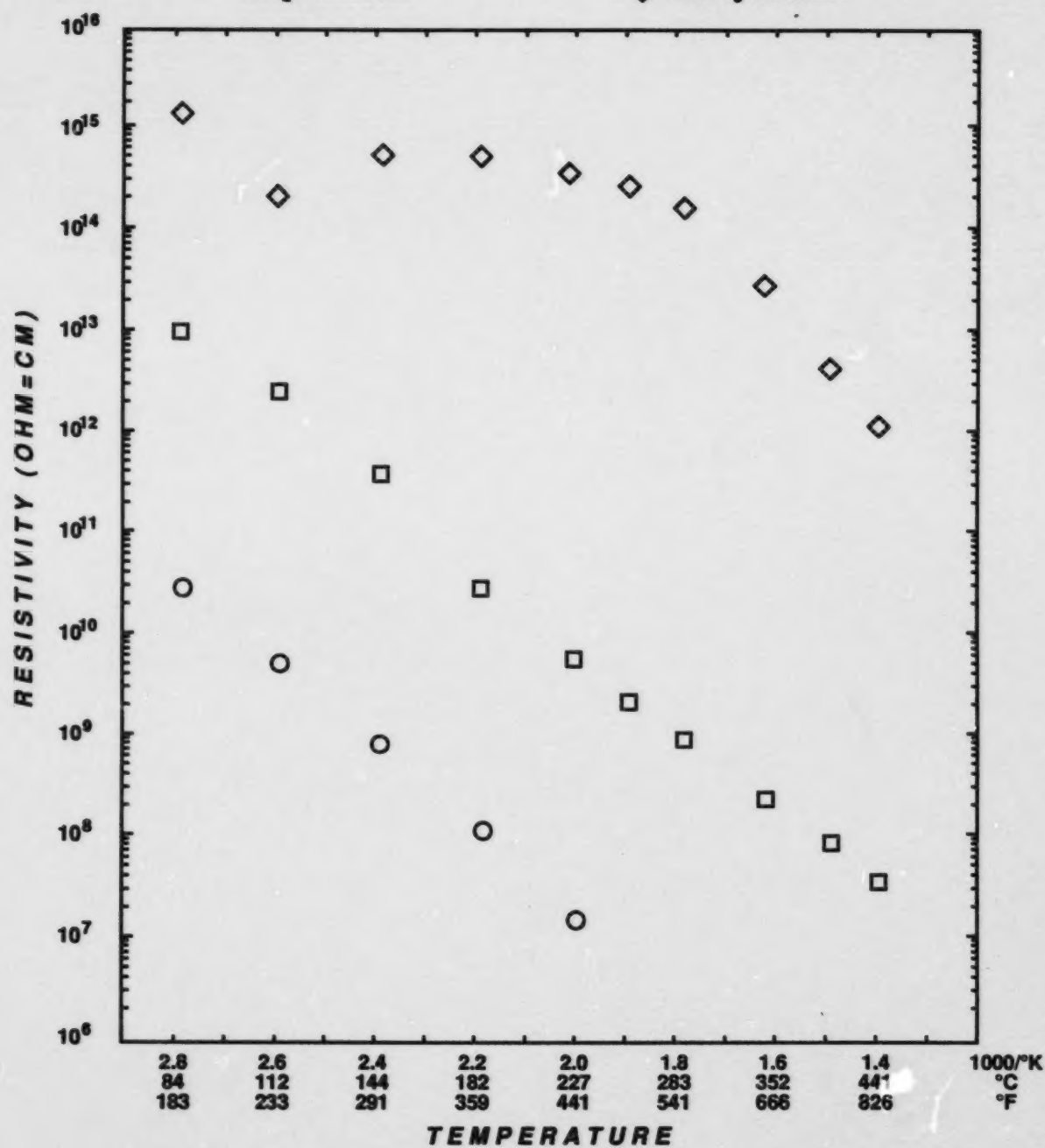


FIGURE 4

PROJECT: 5901
DATE: 9/4/85
% H₂O: 3.30

○ HYDRATED LIME
□ DIATOMACEOUS EARTH
◇ NaHCO₃ SORBENT

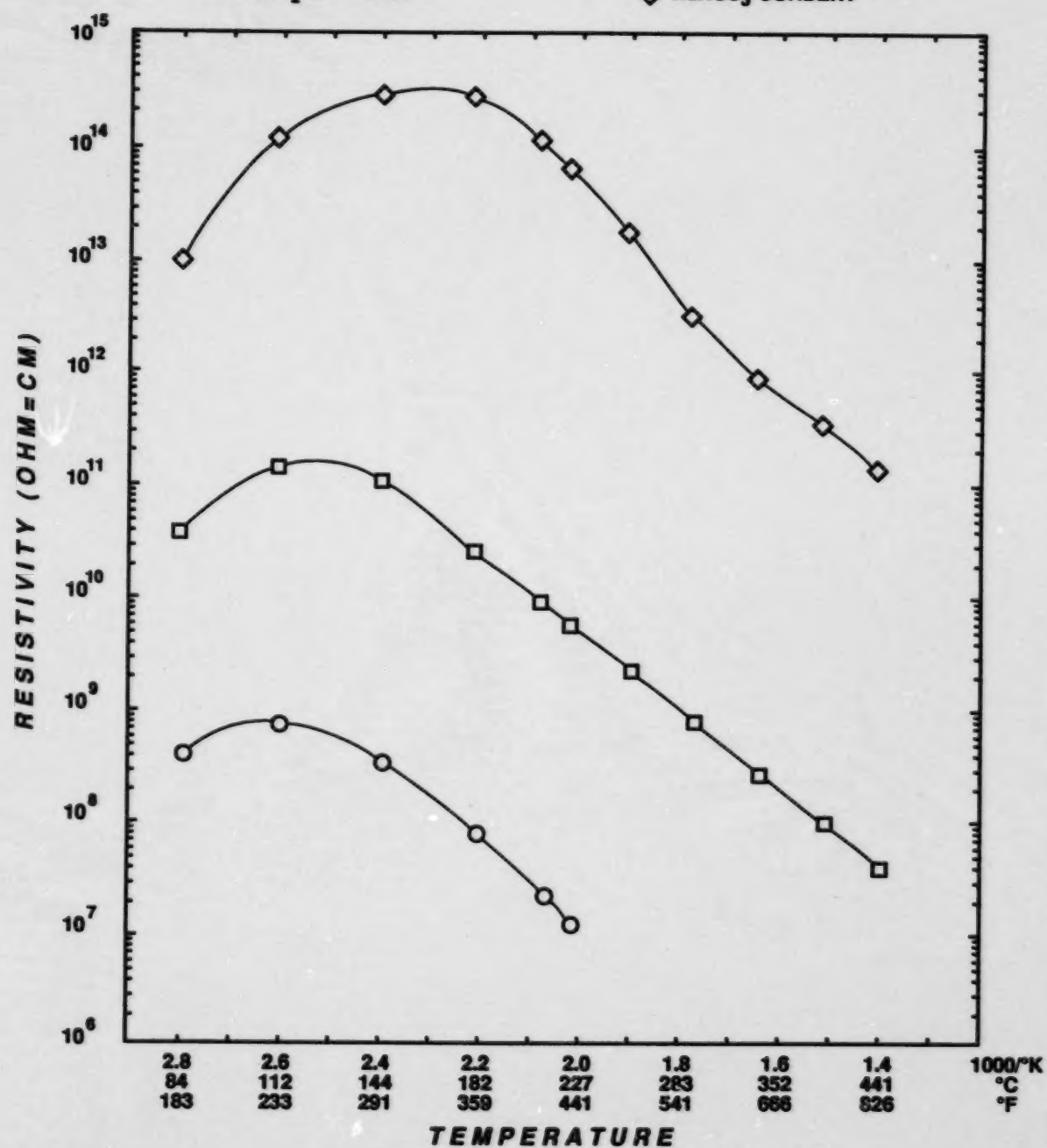


FIGURE 5

PRESSURE DROP

MHD Test Stand — EDSS

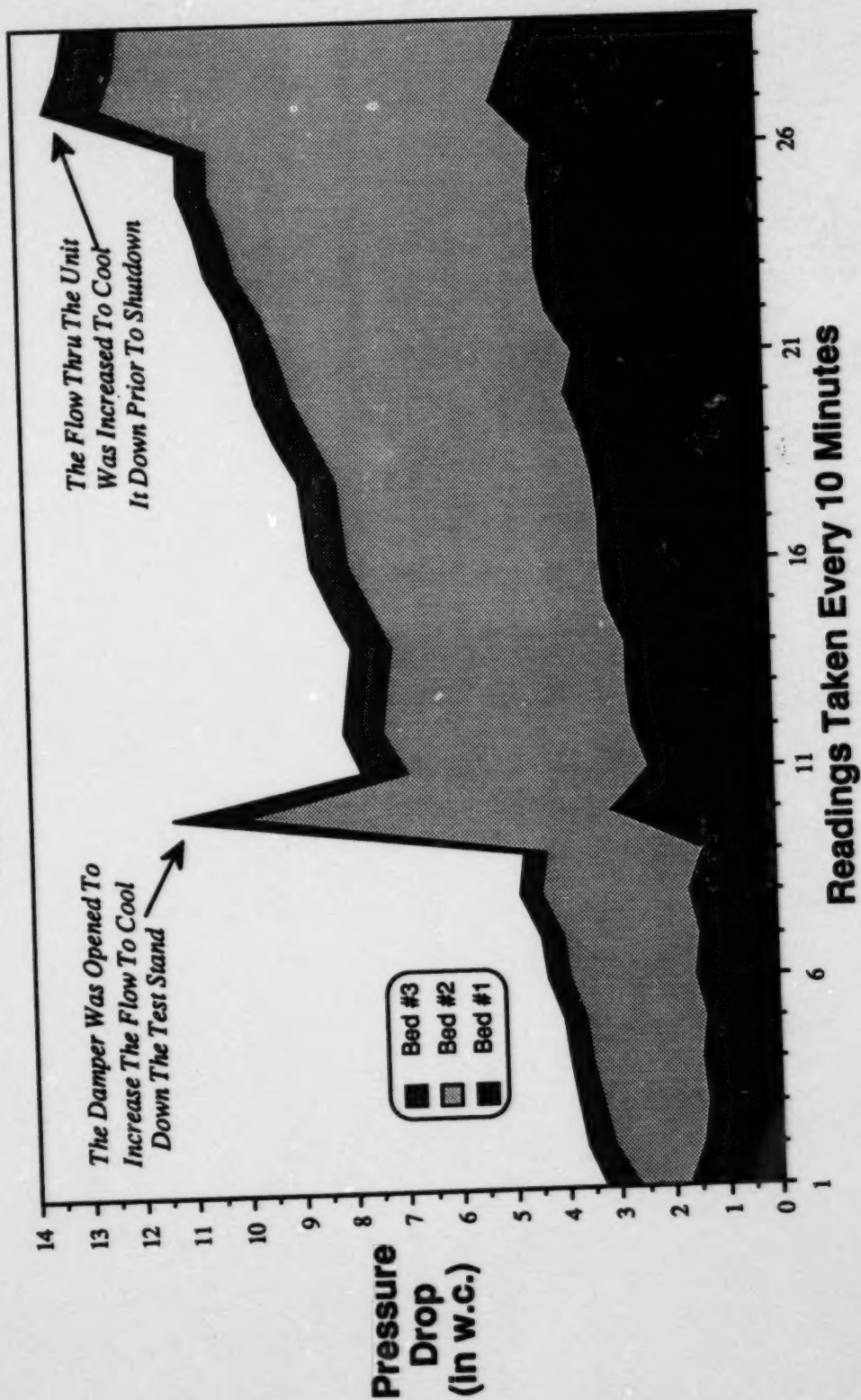


FIGURE 6

Sample Point Layout

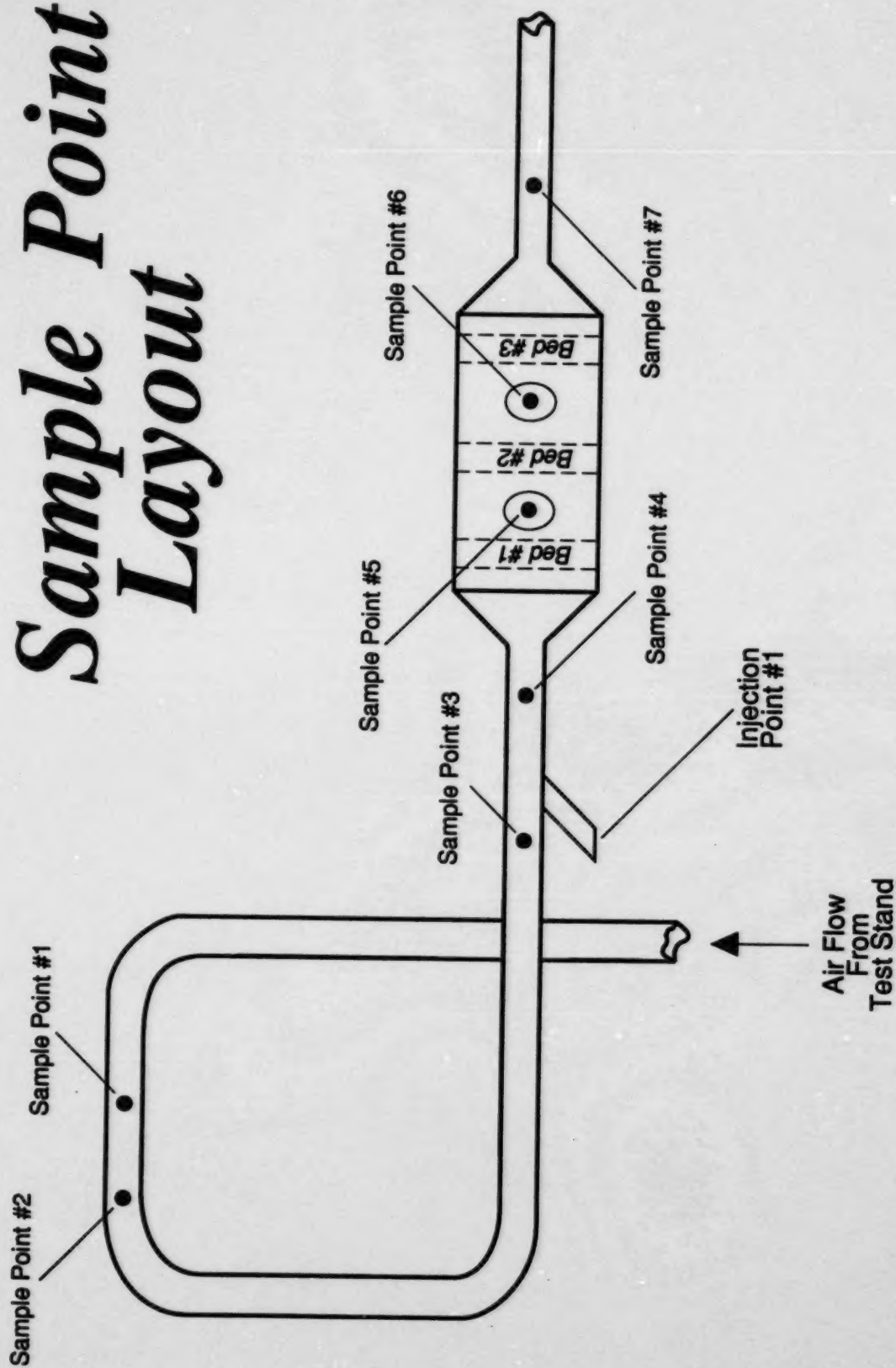


FIGURE 7

SO₂ CAPTURE IN A COAL-FUELED GAS TURBINE SYSTEM

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ABSTRACT

Sulfur dioxide capture at short residence times was investigated in an entrained flow reactor to determine the efficacy of dry sorbent injection in the combustor as a means of reducing SO₂ emissions in coal fired gas turbines. The sorbents examined were commercial grade hydrated limes, calcitic and dolomitic. Effects of temperature, SO₂ concentration and residence time on SO₂ capture were measured for each sorbent. Results show significant SO₂ capture at atmospheric pressure for residence times ≥ 20 ms, with capture at 1100°C and [SO₂] = 1000 ppm being 37 and 65 percent for calcitic and dolomitic sorbents, respectively. The rather steep temperature dependence over the range of 900 to 1100°C indicates the importance of the point of injection on sorbent performance in practical systems. If added sorbent does not exacerbate deposition of solids on turbine blades or combustor walls, dry sorbent injection can be an effective means of removing SO₂ in coal fired gas turbine systems.

BACKGROUND

Direct coal-fired gas turbines (CFGF) are being developed for future utility and industrial power generation applications. Using U.S. coal (beneficiated and micropulverized) as the primary fuel for these units will become attractive if the cost of distillate oil and natural gas increases relative to coal.

However, firing coal instead of the conventional premium fuels could lead to increased pollutant emissions. Coal, even after beneficiation, contains significant quantities of sulfur and ash which may lead to emissions of SO₂ and particulate matter in excess of current EPA new source performance standards. Increasingly

stringent requirements for reduction of acid rain precursors in the future will also increase the need for cost-effective emission control technology. PSI Technology Co. (PSIT) has teamed with General Electric Company (GE) to determine the feasibility of applying SO₂ removal technologies previously developed for utility boiler systems to advanced CFGT-cogeneration systems.

Currently, a cost-effective means of removing SO₂ from coal-fired boiler flue gases is via reaction with calcium-based sorbents: limestone, hydrated lime or hydrated dolomitic lime. These sorbents may be injected into either the combustion chamber or into the duct downstream of the furnace. Of the two methods of SO₂ reduction, injection into the combustor is preferred for application to gas turbine systems since the high pressure in this region (10 to 30 atm) provides the opportunity to capture SO₂ at a higher partial pressure relative to the exhaust. However, the desirability of reducing SO₂ emissions in the combustor, must be balanced against potential erosion of and deposition on turbine blades caused by sorbent particles added to the gas stream.

Many experimental studies have been performed to investigate SO₂ capture by calcium-based sorbents. These studies range from bench and laboratory-scale determinations of sulfur sorption as a function of particle size, surface area, temperature and additives (1-5), to pilot and full-scale determination of sulfur capture (6-10). However, emphasis has been on application to boiler systems, characterized by long residence times (250 to 1000 ms), low pressure (1 atm), and high SO₂ concentrations (1000 to 3000 ppm). The advanced coal-fired gas turbine systems being investigated for coal applications by GE produce power more efficiently when operated at high firing temperatures, and the overall residence time in the high pressure combustion region is about 20 ms. Thus, a complete characterization of SO₂ capture by sorbents in CFGT systems involves measuring the effects of SO₂ concentration, residence time, temperature, sorbent type and pressure. Particular concern centers on extension of the data base to residence times in the 20 ms range.

The objectives of the subject program were to quantify the capture of SO₂ by calcium-oxide based sorbents under conditions representative of anticipated coal-fired gas turbine operation and to utilize the data and validated analytical models to facilitate the practical application of this technology to control of SO₂ emissions for coal-fired gas turbines being developed by GE. To achieve these objectives, PSIT has undertaken a combined experimental and modeling program to measure sulfur removal efficiency at atmospheric pressure, and to predict performance at the higher pressures of gas turbine systems via the pore tree sulfation model developed at PSIT. The pore tree sulfation model has been validated for its ability to predict sulfation at higher pressure under a previous project at PSIT.

In order to characterize SO₂ capture by calcium-oxide based sorbents, measurements of sorbent performance as a function of temperature, residence time, SO₂ concentration, gas-solid mixing, and sorbent type (calcitic versus dolomitic) were made in an entrained flow reactor. In addition, experiments to determine the effects of sorbent pre-calcining and coal combustion products on SO₂ capture by sorbents were performed. This paper summarizes the results of this test program.

SORBENT CHARACTERIZATION

The sorbents used during this test program are described in Table 1. They include both calcitic and dolomitic hydrates used in previous EPA and EPRI-sponsored programs. Initial surface areas ranged from 10 m²/g for a Type-S dolomitic hydrate obtained at a local building supply store to 21 m²/g for a Genstar dolomitic pressure hydrate. These surface areas could be drastically increased by precalcining the sorbent in air at 100 to 400°C for 1 to 8 hr. Precalcines were tested to see whether initial surface area (previously shown to have a small effect on sulfur

capture at long residence time (13)) is more important when the overall time for sulfur sorption is limited to 20 ms. We postulated that at short residence times, the time required to calcine the sorbent after introduction into the combustor may be a large fraction of the total residence time, thus limiting the reaction time available for sulfation.

The majority of the tests were performed with either the Genstar or Linwood sorbents. These two sorbents are very different. Genstar is a dolomitic pressure hydrated lime comprised of 58 percent Ca(OH)_2 and 42 percent Mg(OH)_2 , while Linwood is 94 percent Ca(OH)_2 . Although the crystal structure is the same (face centered cubic) for both materials, Genstar has a somewhat more open pore structure. The Genstar has 80 percent porosity compared to 50 percent for Linwood, and a larger average pore size than Linwood; 15 nm versus 10 nm as determined by nitrogen porosimetry. In addition, the Genstar particle size distribution is smaller than that of the Linwood sorbent as shown in Table 2.

EXPERIMENTAL

MODIFIED ENTRAINED FLOW REACTOR

The apparatus used in this study is shown schematically in Figure 1. For this test program, the facility was modified to include a multipurpose coal/gas burner, a Venturi to improve mixing between the gas and the sorbent, a phase discrimination probe to rapidly separate gas and solid phases in the sample extraction system, and a solids sampling system. The apparatus is modular in design, allowing for easy interchange of sampling and injection probes to provide maximum flexibility. The heart of the apparatus is the entrained flow reactor, a three-zone, electrically heated furnace with a mullite liner. Each of the three zones is independently controlled to allow temperature profiles to be controlled in any chosen reactor configuration.

The combustion products were provided by a horizontally mounted burner which is capable of operation in three modes:

1. Simulated combustion gas with no flame
2. A methane-air flame with added SO_2
3. A methane-supported coal flame with option of added SO_2 (to vary SO_2 levels over that possible with coal alone).

Sorbent injection was achieved by an insulated, water-cooled probe mounted vertically in the reactor. Sorbent was dispensed from a variable-speed auger feeder into an airflow which entrained the particles, carrying them through the injector and into the reactor. This sorbent-injection airflow was typically 2 to 3 percent of the total gas flow through the reactor. A wide range of injection rates was made accessible by varying airflow, auger speed or auger size. A similar auger feeder arrangement was used to carry pulverized coal to the burner.

Feed rates were measured by capturing the solids for a predetermined time period and weighing the sample. For preset auger speed and air flow rate, sorbent feed rates were found to be repeatable to within 1 to 2 percent.

To ensure complete mixing of the sorbent and gas phases, sorbent was injected into the inlet of a Venturi section mounted in the furnace. The turbulence in the contraction and expansion sections of the Venturi facilitated complete sorbent-gas mixing. The sampling probe was inserted below the Venturi to remove gas/sorbent at short residence times. The separation distance controlled the residence times. The sampling probe used in this work is a phase discrimination probe (PDP) surrounded by a water-cooled protective jacket. The probe, shown schematically in Figure 2, effectively separates the solid and gas phases by forcing the gases through a

360 deg turn before they pass into the dryer and filter on their way to the gas analyzers. Further, the water cooling permits very rapid quenching of the gas phase sample, thus precluding further reaction before gas (SO_2) analysis. By use of this probe, we were able to perform gas phase measurement of SO_2 capture at very short residence times following sorbent injection. The actual residence time for a particular experiment was determined by thermocouple measurement of the temperature profile at the probe inlet and measurement of the flow rates. An example of this measured profile is shown in Figure 3.

Gas analysis was performed by a battery of analyzers; SO_2 by UV absorption, CO_2 and CO by non-dispersive infrared analyzers, and O_2 by an electrochemical cell technique. Analyzers were calibrated with premixed gas standards at least twice daily, normally at the start of experiments and at random times during experiments.

Particles were sampled by capturing them in a Pyrex wool-packed trap placed at the exit of the phase discrimination probe. All samples lines were heated to maintain H_2O in the gas phase until after sampling of particulate matter was accomplished.

EXPERIMENTAL PROCEDURE

A typical experiment consisted of instrument calibration before the experiment, checks to ensure that the sampling system was operating correctly, and finally, data collection. Data points were taken in no specific order e.g., for a plot of SO_2 capture versus calcium-to-sulfur ratio, points at high and low sorbent loadings were taken randomly to ensure that there was no effect of regularly increasing or decreasing calcium-to-sulfur ratio. Likewise, repeat data points were collected at random calcium-to-sulfur ratios. Random calibration checks were performed. A standard check on system integrity was performed by introducing a measured amount of SO_2 into the system before starting each day's runs. This procedure assured that there was no progressive degradation of the system.

DISCUSSION OF RESULTS AND CONCLUSIONS

The key issues relative to the use of calcium-based sorbents to remove SO_2 from the combustion products in a GE LM-500 combustor have been addressed during this study. Questions to which this study is addressed include:

- Is it feasible to expect 50 percent sulfur capture by calcium-based sorbents at short residence times (~20 ms) typical of the coal-fueled gas turbine combustor?
- How do properties of the sorbents influence the level of sulfur capture achievable at these short times?
- How much will sorbent reactivity be enhanced at elevated gas pressures typical of gas turbine combustors?
- How will the operation of the gas turbine influence sulfur capture, and how will sorbent injection affect gas turbine operation?

The sections that follow discuss the results and conclusions in terms of these key issues.

EFFECT OF MIXING ON SO_2 CAPTURE

The rate of solid-gas mixing plays an important role in determining sulfur capture by sorbents at high temperatures. The effects of mixing were explored during this test program during long residence time baseline tests. The results are

shown on Figure 4. Percent SO_2 removal was measured as a function of Ca/S ratio at 1100°C , an initial SO_2 concentration of 500 ppm, and a mean bulk gas residence time of 500 ms. First the test series was performed while sorbent was injected into a laminar flow field produced in the reaction tube. Subsequent tests were run over a similar range of Ca/S ratios with a Venturi section located in the reaction tube to induce turbulence and rapid initial mixing.

It can be seen that the improved mixing rate resulted in a substantial increase in SO_2 removal. This has important implications for practical systems. Injection of sorbent through the burner of a coal-fueled gas turbine is probably best represented by Venturi-type mixing. Injection of sorbent downstream of the burner may be better simulated by the slower mixing. Since the objective of our program was to explore the maximum SO_2 removal potential in gas turbine systems, all short residence time tests were performed with the Venturi in the reactor.

RESIDENCE TIME DEPENDENCY

Figures 5 and 6 show utilization as a function of residence time for the Genstar and Linwood sorbents, respectively. For the Genstar pressure-hydrated dolomitic lime (PHDL), there is virtually no dependence of utilization on residence time within the error bars of the measurements. This is true for low (500 ppm) as well as high (1000 to 3000 ppm) SO_2 concentrations at Ca/S = 2.0 and $T = 1100^\circ\text{C}$. This suggests that the rate of reaction is very fast, that the pores fill quickly, and that diffusion of SO_2 through the product layer to form additional product is very slow at long residence time for Genstar PHDL. Effectively, most sulfation occurs before $\tau = 20$ ms.

On the other hand, the Linwood data exhibit a somewhat different behavior. Our data, as shown in Figure 6, demonstrate no dependence of utilization with increasing time up to 100 ms residence time, similar to the Genstar. However, as shown in Figure 5, the longer residence time data of Milne and Pershing (14), and Muzio et al. (12), suggest a slight rise in utilization over the 100 to 1000 ms range. We performed no systematic study to explain this effect since our primary interest was the short residence time region. However, we could hypothesize several explanations for this behavior.

This behavior may be explained by the difference in particle size distribution between Genstar (MMD = $1\text{ }\mu\text{m}$) and Linwood (MMD = $2.5\text{ }\mu\text{m}$). Larger particles (Linwood contains particles as large as $200\text{ }\mu\text{m}$ in diameter) may crack or fracture after long exposure to the high temperature environment in the reactor, producing fresh surface for SO_2 capture. At early times, reaction of these large particles with SO_2 is diffusion controlled and may provide resistance to SO_2 diffusion into the particle. Some evidence for this is presented in Figure 7, a replot of some of the data of Milne and Pershing (14) showing the difference between unsized Linwood (Δ) and Linwood from which particles larger than $7\text{ }\mu\text{m}$ have been removed. These particles comprise 10 percent of the sorbent while removing them results in a 25 percent increase in SO_2 capture at short residence times but no enhancement at longer residence times. A comparison of particle size distribution for Linwood and Genstar before and after reaction with SO_2 is thus seen to be important in unraveling the mechanism by which SO_2 is captured by CaO-based sorbents.

Alternatively, we could speculate that the reaction of SO_2 with Linwood sorbent may indeed be slightly less kinetically controlled than with the Genstar. Therefore, the utilization is always lower, and the SO_2 diffusion through the pore structure at later time is more apparent and important to achieving high utilization in this lower porosity, larger particle sorbent.

In evaluating sulfur capture at residence times characteristic of GE gas turbine combustors (~20 ms), consideration must be given to the following rate processes:

- Mixing rate
- Sorbent reaction rate with SO_2
- Rate of surface area change of sorbent as a result of sintering/grain growth.

As stated previously, in order to achieve maximum sulfur removal, the time to disperse the sorbent uniformly into the combustion gas stream must be short. This may best be achieved by incorporating sorbent into the coal-water fuel or by injection into the primary combustion zone. This guarantees intimate mixing, but the sulfation reaction will not begin until the combustion products are quenched below 1150°C . If the cooling/dilution air is injected late, the sulfation reactions may be limited by two factors:

- 1) The sorbent surface area, which appears to increase drastically with high particle heat-up rates, can subsequently decline due to surface annealing or grain growth before sorption begins;
- 2) The residence time at 1100°C may be only a small fraction of the overall combustor residence time, thus limiting the reaction time. At this point our best guess at the minimum time required for complete sorbent reaction is about 20 ms, based on model calculations as well as experimental results.

For other gas turbine injection schemes, non-ideal or slow mixing of sorbent and gas is a concern. One handy sorbent injection location could be the nutshelling port. The advantage of this location is the temperature profile which is expected to be uniform and could be controlled at 1100°C . However, given the current LM-500 configuration, this port is probably located too close to the combustor outlet to achieve adequate reaction time.

This deficiency could be corrected, however, by small changes in the LM-500 configuration. Either a special sorbent injection port could be installed at the point of dilution air injection, or the combustor length could be extended to provide an additional 5 to 10 ms residence time beyond the nutshelling port. A conservative approach would be to locate the sorbent injectors as far upstream as possible in order to inject at the optimum temperature of 1100°C , and extend the combustor as little as possible in order to achieve 20 ms residence time for reaction.

The hydrated lime sorbent could be injected as a slurry with water or as a dry powder conveyed with compressed air. Practical issues relative to the injection scheme include not only the rapid dispersion of sorbent and combustion products, but also the effects of the injection stream on combustor temperatures and flow patterns, and the production of finely divided sorbent particles (prevention of sorbent particle agglomeration).

SORBENT SELECTION

The test results at a residence time of 20 ms indicate that either a calcitic or dolomitic hydrated lime can achieve 50 percent sulfur capture in a gas turbine combustor (10 atmospheres pressure) at a Ca/S ratio of two. The key sorbent specifications appear to be an initial surface area greater than $15 \text{ m}^2/\text{g}$ (less important), and a mass mean particle diameter of about one micron (more important). Precalcination of sorbents to achieve initial surface areas of 30 to $100 \text{ m}^2/\text{g}$ is unnecessary and may be counter-productive.

Apparently, high temperature calcination within the combustor is rapid (relative to the sulfation reaction) and provides a high-surface CaO product. If the calcination did not occur rapidly, the time remaining for sulfation could limit the extent of reaction within the combustor. The experimental evidence shown in Figure 8 indicates that sulfation was the same (or less), regardless of whether the starting material was Ca(OH)_2 or CaO .

The sulfation reaction (sorbent utilization) depends on both the surface area and porosity of the sorbent as reaction proceeds. Precalcining the sorbent at lower temperatures ($<400^\circ\text{C}$) for long periods of time (8 hr) may in fact lead to grain growth and residual porosity that limits the surface area achievable within the combustor.

As stated before, particle size is the most important sorbent property for maximizing sulfation under gas turbine conditions. Therefore use of a surfactant during hydration to prevent sorbent particles from agglomerating may increase the sulfur capture achievable with a particular sorbent. Tests were run toward the end of the experimental program with a commercially available calcitic lime (Marblehead) prepared using a surfactant. No data are available for this sorbent prepared without surfactant for comparison, but sulfur capture was less than it was for other calcitic limes tested in this program as shown in Figure 9. Without data, it is suspected that even though particle agglomeration may be reduced, the particle size distribution of the Marblehead material is probably coarser than the other limes tested.

PRESSURE EFFECTS

All testing during this project has been performed at atmospheric pressure. However, the effect of combustor pressure on sulfur removal can be accurately predicted using the PSI pore tree model. The model assumes that the initial intrinsic reaction is first order in SO_2 concentration. As shown in Figure 10, this assumption results in an apparent reaction order of ≈ 0.4 due to decreasing surface availability as sorbent surfaces coat or fill with CaSO_4 product. The experimental data obtained at 20 ms residence time also show a fractional dependence of sulfur removal on SO_2 concentration. The experimental reaction order, given the uncertainty in the measurements, was 0.50 ± 0.15 .

The essence of the pore tree model is a description of the sorbent pore structure as a set of "trees" of various sizes whose trunks are located at the particle surface. The branches of the tree describe a progression of pores ranging from a minimum radius of the order of tens of Angstroms to a maximum which is a significant fraction of the particle radius, for which the distribution of pores of radius r_p is proportional to $(1/r_p)^3$. The transport equations include effects of bulk diffusion to the particle surface, continuum diffusion within the large pores and Knudsen diffusion within the small pores. The model calculates the proportion of SO_2 removal controlled by each of these processes and by chemical kinetics at the pore walls. The intrinsic rate constant, k , the particle radius, porosity, internal surface area and mass fraction of SO_2 in the ambient gas stream are required inputs to the model which yields the reactivity as a function of time and temperature and has been extended to include effects of product deposits. A more complete discussion may be found in Ref. 12.

The particle average radius, porosity and surface area are obtained via sedigraph measurements, nitrogen or mercury porosimetry and BET measurements, respectively, while SO_2 concentration and temperature are determined by experimental conditions.

The rate constant, however, must be estimated from experimental data. The procedure for estimating the rate constant used in predictions of short residence time SO₂ capture is explained below.

The pore tree model, as currently configured, uses an initial rate constant, k , for the reaction of SO₂ with the virgin surface of the sorbent (12). As the reaction proceeds, this constant is modified to reflect the slower rate of reaction due to the buildup of product CaSO₄ on the sorbent surface. The virgin surface rate constant cannot be measured directly from existing data. However, determining the functional form which best represents the data currently available allows a prediction of the rate constant at very short residence times to be made.

The data obtained in this test program, combined with longer residence time data¹⁴ from the literature, yielded rate constants that could be fit to the form

$$k = a \tau^{-B}$$

where τ = residence time, and a and B are constants derived from the data. This equation, of course, implies k is infinite as τ approaches 0, so a cutoff of 0.5 ms was arbitrarily selected to determine the initial rate constant to be used in the model. The data used to estimate the initial reaction rate are presented in Figure 10. This fit produces rate constants of 1.8 g SO₂/cm²·s·atm SO₂ at 0.5 ms and 1×10^{-3} at 1.0s. This increase of three orders of magnitude upon decreasing residence time from 1.0 to 0.0005s mirrors recent results obtained at Morgantown Energy Technology Center for adsorption of SO₂ on single crystal CaO which indicate that the rate constant for SO₂ reaction with the virgin surface of CaO is approximately four orders of magnitude greater than rate constants derived from long residence time sorption studies (15).

To determine reaction order, the model predictions can then be plotted in the form:

$$X_{SO_2} \text{ capture} = k[SO_2]^m$$

where m is the apparent reaction order. The model predicts $m \approx 0.4$, depending on the temperature. These predictions are given in Figure 11 for temperatures of 1000 and 1100°C and a residence time of 20 ms, and compared to data obtained at 1 atm pressure. This prediction shows that pore filling/plugging still dominates the reaction rates, even at residence times typical of the GE LM-500 combustors. However, significant capture of SO₂ is still possible at elevated temperatures and pressures due to the rapid rate of the initial sulfation reaction which is directly proportional to the local SO₂ partial pressure.

In applying these data to the LM-500 coal-fueled gas turbine combustor, one must know the local SO₂ concentration and temperature. In the burner zone, combustion takes place under moderately fuel lean conditions so that SO₂ concentrations are less dilute, but temperatures are probably above the CaSO₄ decomposition temperatures dictated by equilibrium. When the combustion products are diluted to about 1150°C, the sulfation reaction can begin. The SO₂ partial pressure at this point will dictate the driving force for the reaction, even if additional air injection/dilution takes place downstream.

Baseline SO₂ emissions from the LM-500 turbine simulator obtained by GE are about 200 to 250 ppm at about 15 percent O₂ in the exhaust gas. This would be equivalent to about 2000 to 2500 ppm initial SO₂ concentration for an atmospheric-pressure test. However, the reaction will start before the exhaust gases are fully diluted. Therefore the initial SO₂ concentration is really equivalent to some number greater than 2500 ppm. At this point there is not enough information available to us relative to the temperature and concentration

distribution in an LM-500 coal-fueled gas turbine to predict the sulfur capture directly from the PSIT data. However, preliminary LM-500 sulfur sorption data can be compared to our model predictions as shown in Figure 12.

In Figure 12 are presented pore tree model predictions of SO_2 capture for Genstar and Linwood at 1100°C , a residence time of 20 ms and 10 atmospheres total pressure for a gas containing SO_2 at a mole fraction of 2×10^{-4} or 2000 ppm in the high pressure region. Also plotted are two experimental points obtained in the LM-500 simulator at GE, one for Linwood at a calcium-to-sulfur ratio of 2.0 and the other for Genstar at the same mass loading of sorbent used with Linwood or a calcium-to-sulfur ratio of ~ 1.2 . Agreement is not good for the Linwood, but acceptable for the Genstar.

There are many potential reasons for agreement or disagreement for these comparisons. First of all, the sorbent in the GE experiments was injected as part of the slurry carrying the coal. This could lead to delayed sulfation due to the vaporization of the water, followed by combustion and sulfur release. It is possible that the sorbent could have agglomerated to present a particle size larger and less reactive than that assumed. Further, the temperature profile in the GE combustor is most certainly non-isothermal. Clearly, this situation is somewhat different from isothermal reaction of a non-agglomerated sorbent.

OPERATIONAL IMPACTS

One concern relative to injection of calcitic and dolomitic hydrates is the potential physical and chemical interaction between coal ash minerals and sorbent particles. The interaction could possibly occur in two ways. First, the sorbent could coalesce with molten coal ash on the surface of burning char particles, especially if the sorbent is incorporated into the coal slurry fuel. This interaction could not only decrease the sorbent surface area available for sulfation, but could flux the aluminosilicate coal minerals to produce stickier particles that are more prone to deposit on turbine blades.

The second interaction could occur due to evaporation of volatile coal minerals and subsequent condensation on the high-surface area sorbent particles. Residual alkali from the coal cleaning process or alkali additives to the coal-water fuel are likely candidates for this interaction mechanism.

As part of this test program, the vaporization-condensation interaction was investigated. Micropulverized, beneficiated coal containing about 1.6 percent ash, of which about four percent was residual sodium hydroxide from the coal beneficiation process, was burned to produce the products of combustion. Sorbent was injected into this gas stream at about 1100°C and the sorbent-gas contact time was about 20 ms. Under these nearly isothermal conditions, there was no effect on sulfur removal efficiency. No solids samples were taken for analysis of alkali surface coating, nor was an alkali balance performed on the system.

Based on these preliminary results, we cannot preclude the possibility of ash-sorbent interactions in the combustor. The impact of these interactions on sulfur capture, however, are expected to be minor. More important is the issue relative to the deposition characteristics of ash-sorbent particles. To fully evaluate this concern, the size and surface composition of particles generated by the ash and sorbent for different sorbent injection schemes must be taken into consideration. This analysis was beyond the scope of the present program, but could easily be performed using the apparatus described herein.

SUMMARY OF RESULTS

- We have found that the sulfation reaction is significantly faster than expected. Initial sulfation occurs on a time scale of less than 20 ms (our experimental sampling limitation) resulting in a sorbent utilization of order 10 to 20 percent. Further increases in utilization occur slowly, depending on sorbent type, on a much longer time scale of order 200 to 500 ms.
- Since sulfation is very rapid, uniform gas-solid mixing in the combustor is essential to optimize SO₂ capture by calcium-oxide based sorbents. It is also important to incorporate mixing schemes that occur on a time scale comparable to the reaction time. Slow or incomplete mixing can decrease SO₂ capture by as much as a factor of two.
- Gas temperature at the injection point is also important, with the highest SO₂ capture occurring at the optimum temperature defined by the balance between sulfate product formation and thermal decomposition (12). While it is possible to achieve higher product formation rates at temperatures greater than 2200 to 2300°F, product decomposition and release of SO₂ will limit the achievable sulfur capture - unless innovative schemes can be devised to quench and remove the sorbent before decomposition occurs.
- At short residence times such as those encountered in coal-fired gas turbine combustors, e.g., 10 to 30 ms, the effect of sorbent particle size on SO₂ removal is more pronounced than at longer times. Using the smallest possible sorbent size increases SO₂ capture and can help to reduce erosion/deposition problems since the smaller particles will more easily follow the gas stream around turbine blades.
- As indicated above, it appears that the majority of SO₂ capture, by micron-sized sorbent particles, takes place within the first 20 ms. This suggests that, for the coal-fired gas turbines which may operate at higher temperatures, sorbent injection further downstream from the flame, but before the turbine may still provide satisfactory SO₂ capture.
- The pore tree model is a useful engineering tool for predicting SO₂ capture by CaO-based sorbents under various operating conditions. Model predictions of 40 to 60 percent capture (20 to 30 percent utilization) at a Ca/S ratio of two for an isothermal scenario of dry sorbent injection are comparable to turbine simulator results (30 to 40 percent utilization) in which sorbent was injected with the coal-water slurry fuel.
- Dolomitic hydroxides are more efficient (on a calcium utilization basis) than calcitic materials with SO₂ captures of 35 and 20 percent respectively at an SO₂ concentration of 500 ppm, temperature of 1100°C, calcium-sulfur ratio of 2, and a residence time of 20 ms. However, this difference in sulfur capture may be at least partially explained by the finer particle size distribution characteristic of the dolomitic hydrates tested during this program.
- Short residence time SO₂ capture by calcium-based sorbents in the high-pressure combustor of a coal-fired gas turbine is a viable means of emission control if the additional particulate loading

e.g., sorbent, does not result in increased deposition or erosion on turbine blades (investigation of deposition was not within the scope of this project).

This program has demonstrated that SO₂ capture by calcium-based sorbents is substantial, even at short residence times and that, barring deposition and erosion problems, this technology can be useful in reducing SO₂ emissions from direct coal-fired gas turbines.

ACKNOWLEDGMENTS

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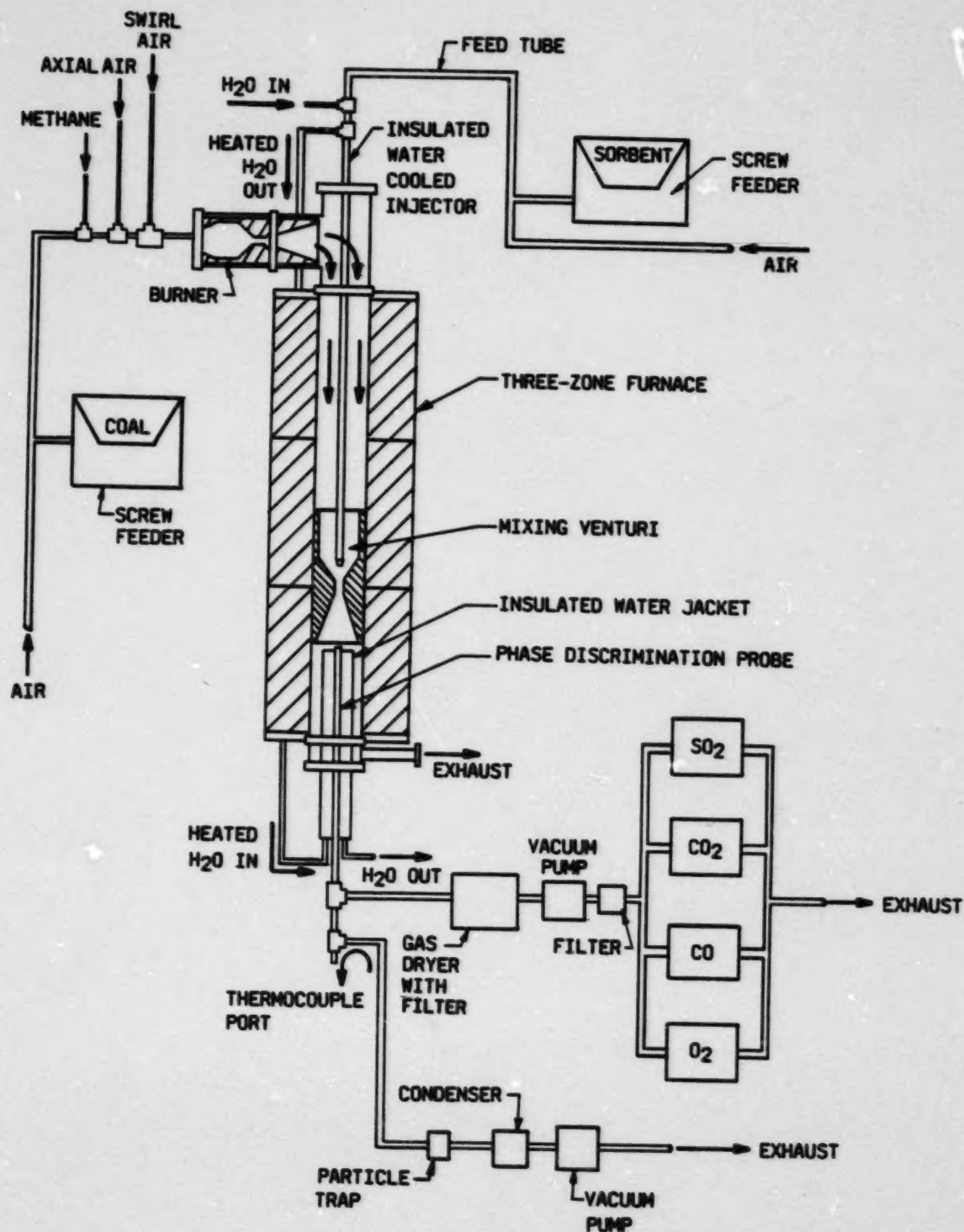
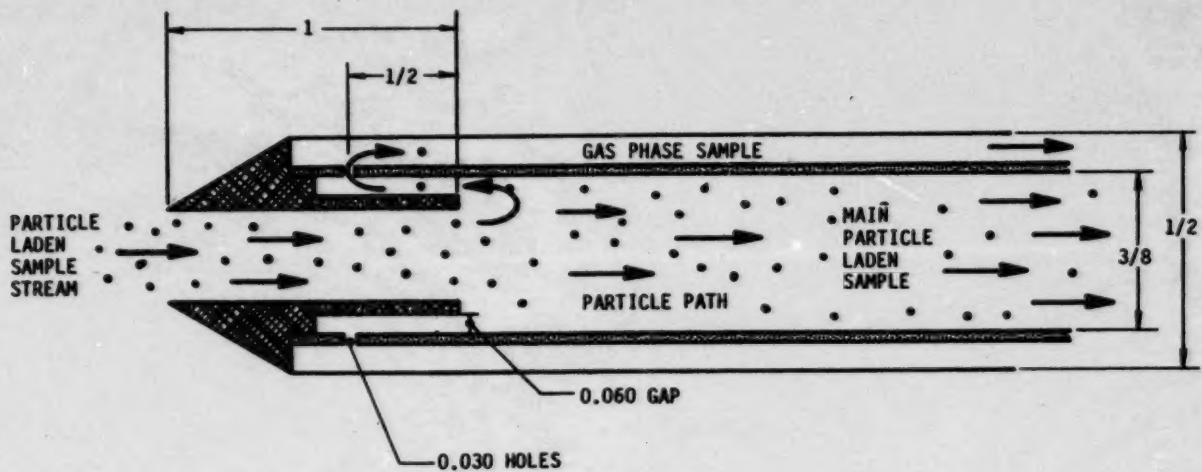


Figure 1. Experimental apparatus.



DIMENSIONS: INCHES

Figure 2. Phase discrimination probe.

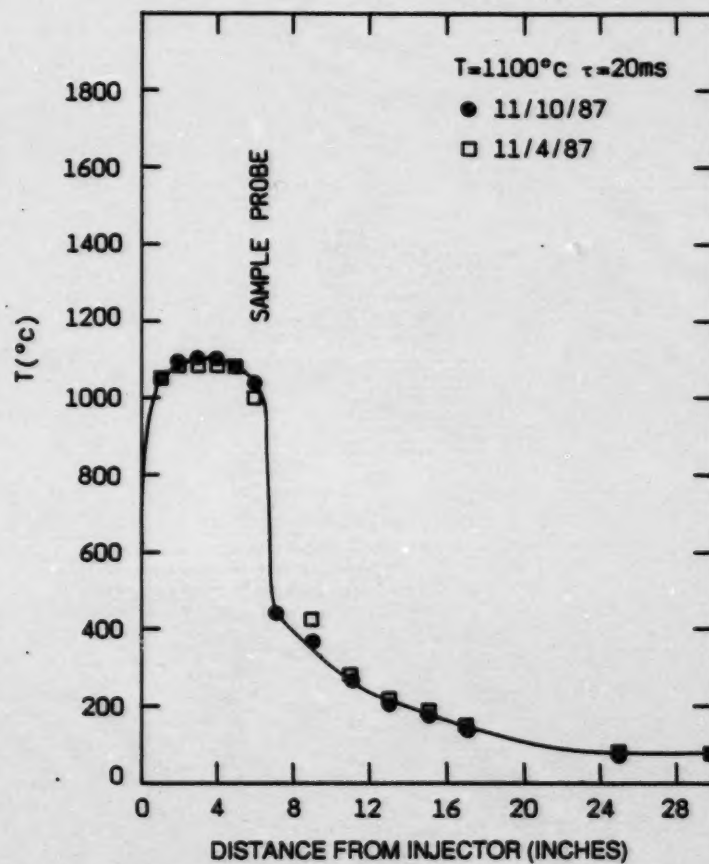


Figure 3. Typical temperature profile.

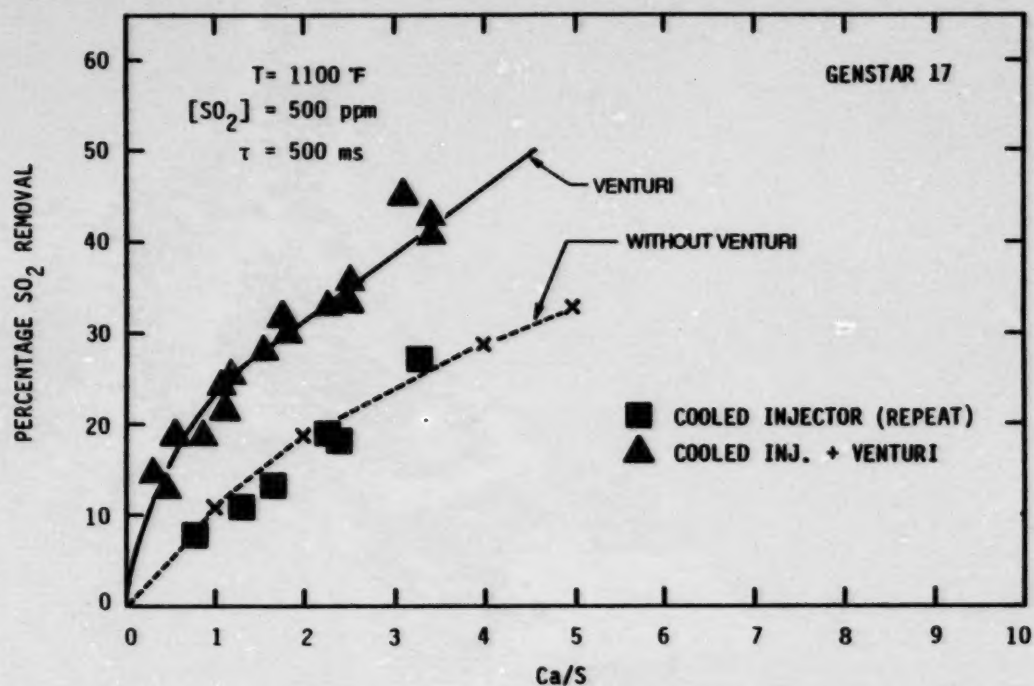


Figure 4. Venturi injection of Genstar.

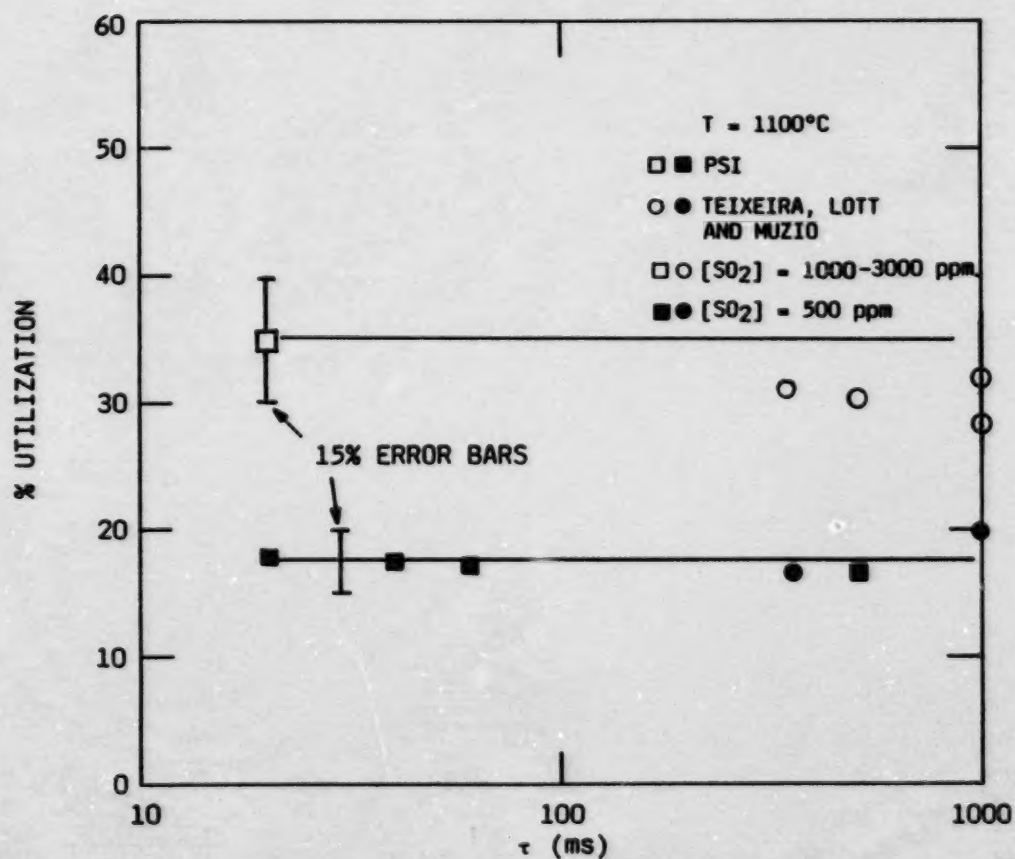


Figure 5. Utilization versus residence time (Genstar).

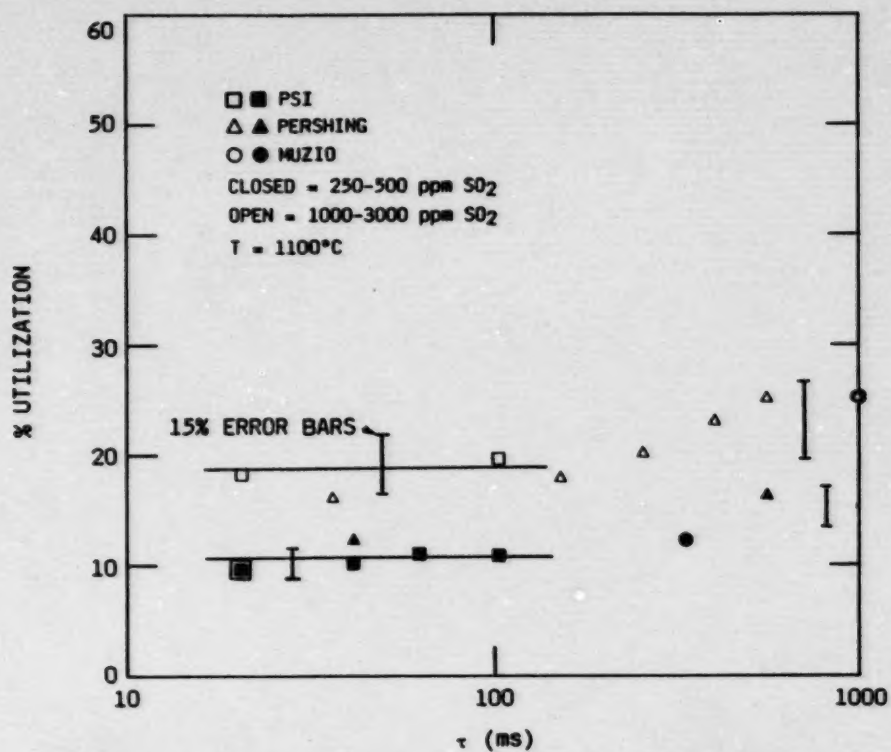


Figure 6. Utilization versus residence time (Linwood).

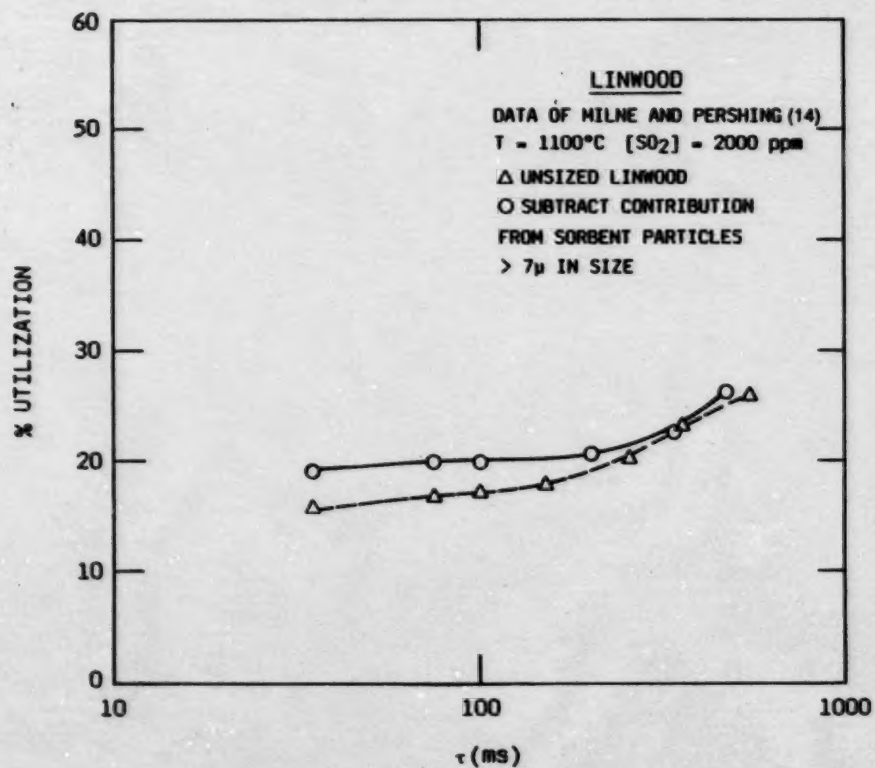


Figure 7. Effect of particle size distribution on sulfur capture.

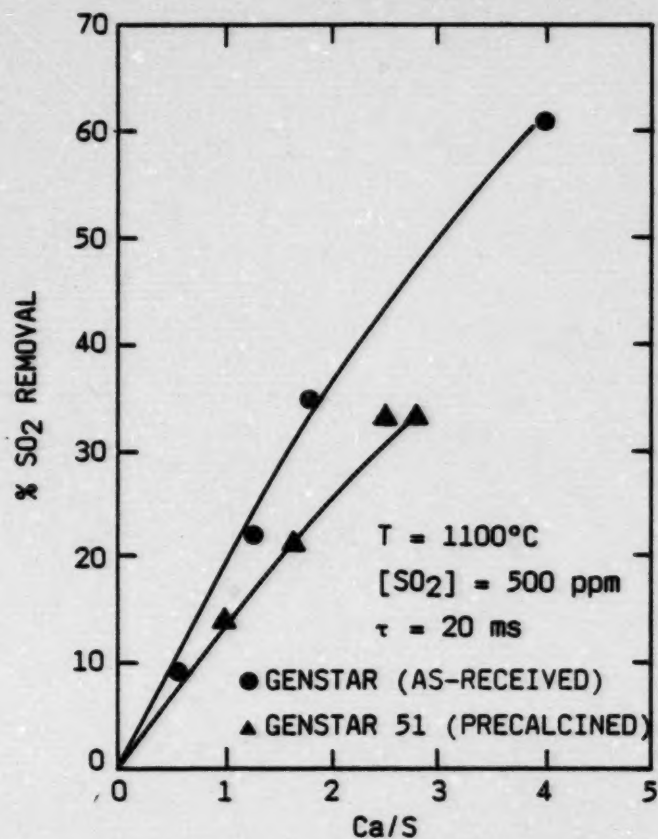


Figure 8. Effect of precalcining.

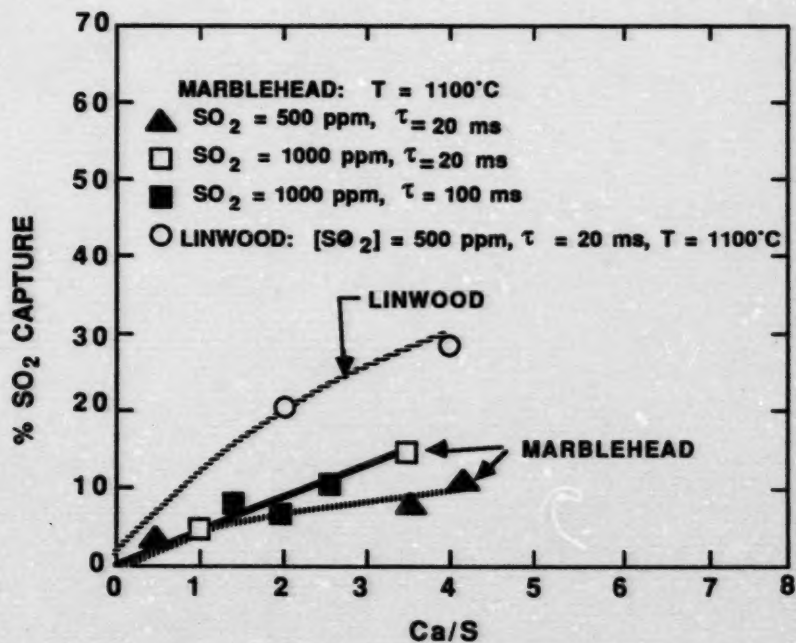


Figure 9. Comparison of Marblehead and Linwood sorbents.

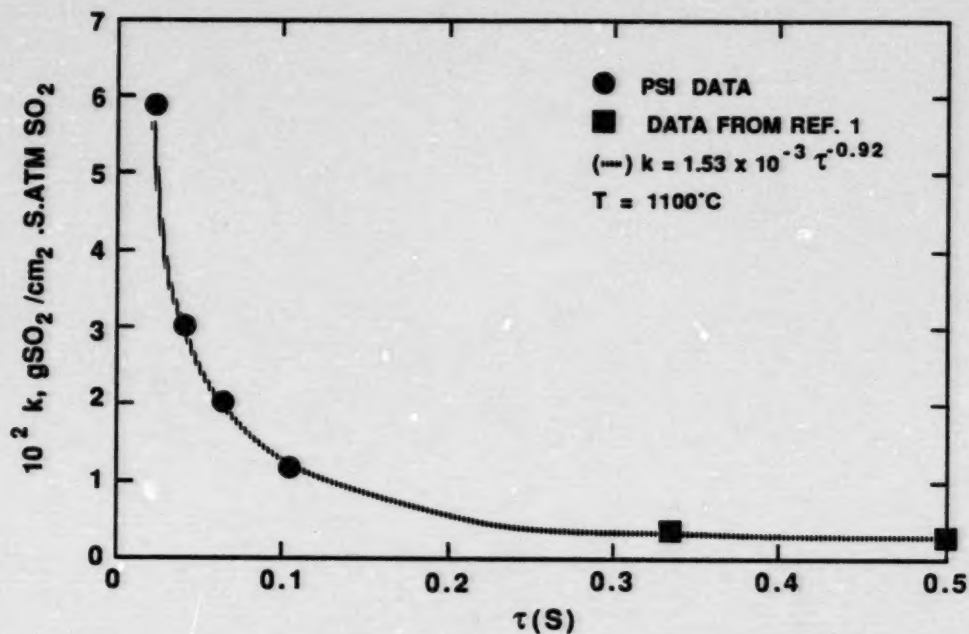


Figure 10. Fit of k versus τ for Genstar sorbent.

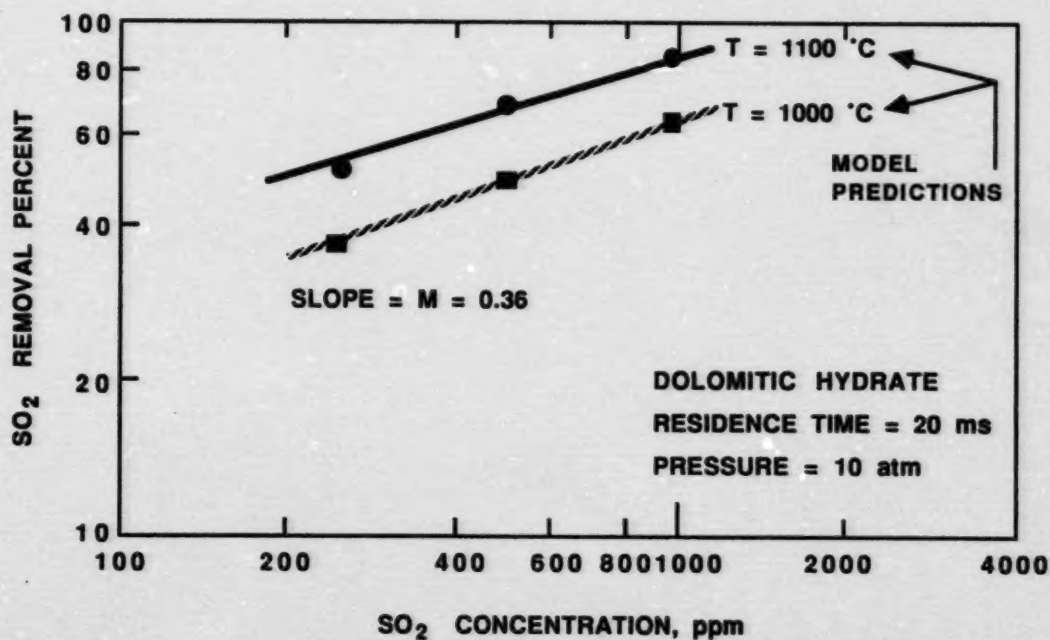


Figure 11. SO_2 concentration dependence predicted by pore tree model.

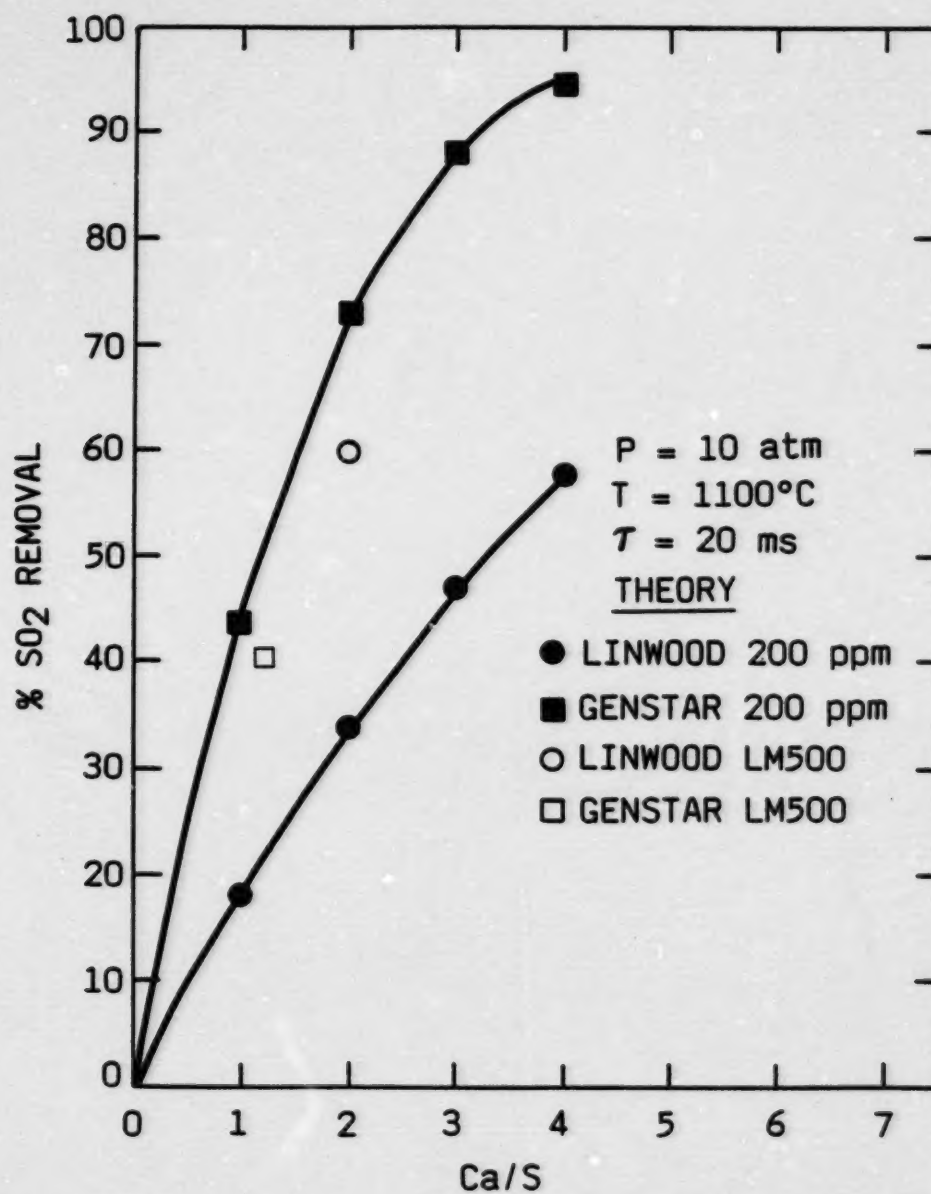


Figure 12. Pore tree model predictions of SO₂ capture compared to results from the GE turbine simulator.

Table 1. Sorbent Properties

Sorbent	Type	Initial Surface Area (m ² /g)	Surface Area After Precalcination in Air (m ² /g)	MMD* (μm)	Porosity
Genstar pressure hydrate	Dolomitic	17-21	60	1.0	0.80
Linwood atmospheric hydrate	Calcitic	13.4	-	2.5	0.50
Longview atmospheric hydrate	Calcitic	16	37	2.5	0.50
Marblehead precipitated hydrate	Calcitic	11	-	-	-
Type-S Hydrate	Dolomitic	10	38-41	~5	-
*Mass Mean Diameter					

Table 2. Sorbent Particle Size Distribution*

Size Range	Linwood	Genstar
< 1 μm	10%	38%
1-10 μm	75%	52%
> 10 μm	15%	10%
*Determined via sedigraph analysis		

FGD SYSTEM COST COMPARISONS

by

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ABSTRACT

The initial cost of an FGD system is a function of the type of system, the waste handling included, and many other factors. Comparing system cost on a dollars/kW basis is only part of the story. This paper investigates the influences that various factors have on four separate bases for cost comparison and proposes improvements for comparison purposes.

An analysis of FGD system cost information supplied to the Federal Energy Regulatory Commission has provided information for the cost comparison. Four categories were compared: Dollars per kW; mills per kWh; dollars per pound of SO₂ removed; and dollars per scfm. Dollars per scfm was found to be influenced by several factors, but not as skewed by the type of system or fuel supply as the other categories.

Dollars per kW indicates the lime systems are generally lower in capital cost than limestone, dollars per kWh is representative of operating costs and in general indicates the limestone system as lowest. The total levelized costs are used for other categories. The dollars per pound of SO₂ removed gives a significant disadvantage to low sulfur coal systems.

This study also provides a reporting of actual costs for on-line FGD systems. This information will be useful in projecting costs for new FGD systems and in comparing alternative strategies for SO₂ removal.

BACKGROUND

As the debate over the cause of Acid Rain developed, the control of sulfur dioxide emissions by utilities emerged as one of the major issues. At the same time, the additional issue surfaced as to how should sulfur dioxide emissions be controlled.

Flue gas desulfurization systems have never been popular with utilities. At many power stations, the operation of the flue gas desulfurization systems have proven less than satisfactory. Utility executives have been faced with sizable expenditures to keep marginal units operable. The life expectancy for these units has been ten to fifteen years. This is not an acceptable period for utilities.

For this as well as other reasons, utilities have supported the development of other means to control sulfur dioxide emissions. These methods include removal of sulfur from the coal prior to combustion, LIMB (Limestone Injection Multistage Burner Technology), fluidized bed boilers, injection of lime or soda ash into ductwork, Laser technology and promising technologies developed in other countries.

Some of these systems are showing remarkable potential. The use of fluidized bed boilers has skyrocketed. Like all new technologies, problems are appearing that require solutions.

If sulfur dioxide controls must be used on a new or existing generation unit, how does the utility escape from the problems that will inevitably occur with a new technology? Further, how can the capital, operating and maintenance costs be determined with a reasonable degree of accuracy?

During the time work was being initiated on alternative control technologies, development work continued on lime/limestone flue gas desulfurization systems. Corrosion and erosion problems were eliminated through the use of better materials. Better design and operation of absorbers limited scaling and pluggage. The use of chemical additives eliminated this problem completely. Better design of mist eliminators limited or eliminated solids carryover. Other improvements were made so that the entire lime/limestone flue gas desulfurization system and the solid waste systems can be operated continuously and maintained economically.

The work on these flue gas desulfurization systems has received limited publicity. The original lime/limestone systems have progressed through the fifteen-year development period normally required to debug a new technology, and these systems have been debugged and improved. They should be considered for a new or retrofit unit.

FGD SYSTEM COST

The range of capital costs for (FGD) systems in the literature ranges from \$40/kW (1) to \$700/kW (2). Similarly, operating costs appear to range from a low of 0.56 mills/kWh (3) to as much as 15.8 mills/kWh (4). The most often quoted numbers are 140 to \$175/kW capital cost and around 3 to 4 mills/kWh operation and maintenance costs.

To improve upon these estimates, we decided to look at historical cost data, and develop current dollar costs based on historical evidence. Baseline data for this study was obtained through the Federal Energy Regulatory Commission (FERC) office in Washington, D.C. Data is available on the capital cost and operation and maintenance cost for most of the utilities operating FGD systems. This data is presented on the FERC Energy Information Administration (EIA) Form 767. The data requested on the form is initially compiled by the utility and input to a computer tape. The computer then generates the completed form in subsequent years for review and update by each utility.

We were able to obtain sufficient data from a computer tape containing the FERC information to identify capital costs and operation and maintenance costs on 127 different units. This included 30 wet lime systems and 67 wet limestone systems. The remaining systems included spray dryers, sodium carbonate systems, dual alkali, Wellman-Lord, and magnesium oxide based scrubbers. The limited number of units in each of these categories did not provide an adequate data base for analysis of these systems. The lime and limestone systems, however, were subjected to further review.

A total of 13,703.3 MW had operating lime FGD systems. Unit size ranged from 156.3 MW to 835 MW. In-service dates ranged from 1974 to 1985. The capital costs were escalated to 1985 dollars based on this in-service date. Capital costs ranged from a low of \$66/kW to a maximum of \$332/kW, less than half of the range observed in the literature, but still a broad range. The average capital cost was \$156/kW. Similarly, operation and maintenance costs ranged from 0.5 to 6.75 mills/kWh. The average O&M cost was 2.50 mills/kWh.

Potential explanations for the wide range of values include the fact that some of the units have waste handling costs and some may be bare system costs. Ductwork with special materials of construction and chimneys may or may not be included in some of the estimates due to different cost accounting practices. On many units, the electric costs for the equipment in the flue gas desulfurization and solid waste systems are not included. There is also a possibility that there may be some units only partially scrubbed, or errors may have occurred in transcribing and entering the data which we have been unable to identify and correct.

The limestone systems offered the largest data base and allowed the opportunity to further differentiate and compare the data. A total of 33,136 MW are served by limestone scrubbers. Unit size ranges from 134 MW to 873 MW. In-service dates range from 1973 to 1986. Initially, we looked at the capital costs which averaged 131 \$/kW. The range of these costs was again rather wide - from 49 to 352 \$/kW. The O&M costs range from 0.4 to 2.9 mills/kWh. The average O&M cost was 1.18 mills/kWh.

These were well below the numbers generally quoted in the literature and the limestone systems were well below the average for the wet lime systems regarding both capital and operating costs. This was an unexpected result, but an interesting surprise. Typically, due to the higher reactivity of lime, the major equipment items are smaller and, as a result, assumed to be less expensive. The fact that limestone systems were actually less on a capital cost basis encouraged us to look at the data more closely.

We divided the limestone systems into packed tower designs and spray tower designs. The spray tower design has been developed to avoid some of the pluggage problems associated with packed towers. The results of the analysis showed that the spray towers were substantially less on a capital cost basis (111 \$/kW compared to 151 \$/kW for packed designs) and on an O&M basis (1.09 mills/kWh compared to 1.25 mills/kWh).

We then divided each group into small size units and large units. The middle, or break point was 450 megawatts. Approximately half the units were less than or equal to 450 megawatts and half were larger than 450 megawatts. According to this data, the smaller units result in lower costs, averaging 104 \$/kW versus 115 \$/kW for units over 450 MW for the spray tower design.

Similarly, the O&M costs were lower for the smaller units. A dramatic reduction was seen in the spray tower designs with units less than 450 MW averaging 0.72 mills/kWh. Units over 450 MW averaged 1.41 mills/kWh. The packed tower design had a much closer cost but still indicated the smaller units as less expensive, averaging 1.21 mills/kWh while the units over 450 MW averaged 1.28 mills/kWh.

As a conclusion, we have taken a brief look at how FGD systems stack up against published costs for fluidized bed combustion, and LIMB or Limestone Injection Multistage Burner Technology.

Fluidized bed combustion has only been applied to units below 150 MW. The published cost for retrofit to an existing facility has been estimated at

approximately 296 \$/kW (5). This same article estimated O&M costs at 0.88 mills/kWh. This compares favorably with FGD units, but does not indicate an overwhelming cost advantage.

Very limited published information was found regarding LIMB technology. This technology would obviously be very low in capital costs, involving only burner replacement, some type of reagent preparation, and possibly some modifications to the ash handling system. In addition, since this technology is only looking at a removal efficiency of 30 to 50 percent, it is not appropriate to compare it with conventional technology except on the basis of dollars per ton of SO₂ removed. Published estimates have indicated this cost could range from 615 to 814 \$/ton (6). The costs for wet lime and limestone systems averaged approximately \$220/ton.

SUMMARY AND CONCLUSIONS

To summarize, capital costs were reported in the literature as 40 to 700 \$/kW and nearly 300 \$/kW for FBC. Our investigation indicates averages below 160 \$/kW for conventional FGD systems. Similarly, O&M costs have been indicated as ranging from 0.6 to 16 mills/kWh, and one study reported operating costs of 0.8 mills/kWh for FBC units. Our review of historic data indicates lime systems averaging approximately 2.5 mills/kWh and limestone systems below 1.10 mills/kWh. On the basis of total levelized cost (i.e., \$/ton SO₂ removed) the conventional systems compare very favorably with the published costs for LIMB technology of 615 to 814 \$/ton.

The general conclusion is that the cost of FGD systems, in general, and the smaller limestone spray tower systems especially, result in actual costs lower than the numbers generally being predicted at this time. The reasons that lower costs are being experienced is a credit to the utilities as well as the consulting architects and engineers who serve them. It is through the efforts of the individuals involved in the design, purchase, and operation of the systems, that costs are minimized.

As familiarity with the systems has been gained, cost saving measures have been found. Most utilities and designers have now eliminated reheat which was costly both in capital costs and also O&M costs. Good contracts have been developed for reagent supplies, the number of operation and maintenance personnel required has been reduced through improved training programs, and good design decisions have led to reliable, dependable systems. Investigations into materials of construction have led to improved operations. A careful selection of spray header materials results in improved system reliability, while another example is pumps with special operating characteristics for waste-handling service have improved the waste-handling operations.

In summary, cost efficiency has been implemented by the owners and operators of FGD systems based on what works. This type of approach to alternative sulfur reduction options has not yet occurred.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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**COMBINED SO_x/NO_x REMOVAL IN A HIGH-SULFUR
SPRAY-DRYER/FABRIC-FILTER SYSTEM**

by

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ABSTRACT

Argonne National Laboratory (ANL) has been conducting research on combined nitrogen oxides (NO_x) and sulfur dioxide (SO₂) control since 1981. Technologies applicable to both retrofit and new installations have been investigated, with particular emphasis on applications involving high-sulfur coal. A major portion of this program has been centered around the spray-dryer/fabric-filter system that provides flue-gas cleanup (FGC) for Argonne's largest, coal-fired boiler. This was the first FGC system of its type to be installed and continuously operated on high-sulfur coal in the United States. Over the last six years, Argonne's research has established that the technology is both effective and economical for control of SO₂ in that application.

Under the combined SO_x/NO_x research program, Argonne conducted two series of field tests on the spray-dryer FGC system. The conditions for the tests were selected on the basis of previous work by Niro Atomizer (using the ANL system), laboratory research at ANL, and intermediate-scale tests at the Pittsburgh Energy Technology Center (PETC). Both changes in process operating conditions and addition of caustic soda (NaOH) to the lime slurry were employed. The results indicated that, under certain operating conditions, it is possible to achieve significant levels of combined control. The addition of NaOH was not essential, but did enhance removal of NO_x. Also, higher levels of SO₂ in the inlet flue gas were found to be beneficial, and changes in particle characteristics that developed in the drying process were found to play a role that has implications for other technologies based on dry sorbents.

INTRODUCTION

Increased control of SO₂ has been the focus of acid deposition debates for many years. Recently, calls for greater control of NO_x emissions have also been heard in response to their implication in environmental damage. The Department of Energy's (DOE) Environmental Control Technology Program addresses these concerns and potential control regulations through program elements dealing with SO₂ Control, NO_x Control and Combined NO_x/SO_x Control. Argonne National Laboratory has conducted research in the latter area since 1981. This work has been focused on high-sulfur systems and has involved both laboratory-scale research and field tests.

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The benchmark for evaluating new process concepts is a combination of selective catalytic reduction (SCR), particulate-matter control, and wet limestone flue-gas desulfurization (FGD). The SCR system, in particular, represents a significant capital cost, potentially high operating costs (for catalyst replacement), and a very difficult retrofit at most installations. Therefore, research in the ANL program has emphasized techniques that can enhance the NO_x-removal capabilities of existing SO₂ control processes. Such an integration simplifies the system and could take advantage of the many scrubbers already in place. For wet scrubbers, high levels of simultaneous removal for NO_x and SO₂ were achieved in the laboratory through progress in the preparation and use of metal-chelate additives. This additive technology (ARGONOX) was recognized by the award of a U.S. patent (1). Additional research in this area is being directed toward further development of an integrated process concept and larger scale tests in cooperation with the Dravo Lime Co.

For the last four years, research in the ANL program has been focused primarily on spray-dryer/fabric-filter FGD systems. Such systems have achieved rapid acceptance by the electric utilities and other industries for use with low-sulfur coal because they offer advantages such as relatively simple process configurations, good operability/reliability, low water and energy consumptions, and production of a dry, easily handled waste. However, the suitability of spray-dryer systems for high-sulfur applications has been questioned on the basis of removal capability and economics. In 1982, ANL began operation of the first commercial-scale (20 MWe equivalent) spray-dryer/fabric-filter system to operate on high-sulfur coal. Since then, we have accumulated a considerable body of information on the operation of this integrated SO₂/particulate-matter control system with coals ranging up to 4.5% in sulfur content and SO₂ removals as high as 95%. This experience has established that the technology is both technically and economically viable for boilers firing high-sulfur coal (2).

In order to integrate NO_x removal with the SO₂/particulate-matter control capability of spray-dryer systems, ANL investigated chemical additives and modified process conditions in the laboratory using a fixed-bed contactor and a small spray-dryer system. Complementary research at an intermediate scale was conducted at the Pittsburgh Energy Technology Center (3). The laboratory work identified several chemical additives that, under certain conditions, significantly improve NO_x removal. However, process conditions such as flue-gas temperature, filter-cake thickness, and SO₂ concentration were also found to be significant. Based on the promise shown in the laboratory and intermediate-scale tests, it was decided to field test one additive -- NaOH -- and several combinations of process conditions in Argonne's commercial-scale system.

Two sets of field tests were conducted and, while the results of the most recent tests are still undergoing evaluation, it is clear that significant levels of combined NO_x/SO_x control can be achieved in spray-dryer-based systems. Some of the results may also be applicable to the various furnace- and duct-injection technologies currently under development. In the following sections of this paper, the Argonne system is briefly described, the test conditions employed are given, the removals attained are presented, and the most significant factors for achieving combined control are identified.

SPRAY DRYER SYSTEM CHARACTERISTICS

Argonne's spray-dryer/fabric-filter system was installed by Niro Atomizer in 1981 as part of a conversion of the site's principal steam-generating boiler back to coal. Significant design features include a rotary atomizer, a pulse-jet fabric filter, and sorbent (lime-based) recycle. A diagram of the system

is shown in Figure 1. The coal supply to the boiler is from the Illinois basin and nominally contains 3.5% sulfur.

The sorbent slurry used in the spray dryer is a blend of recycled solids and fresh milk of lime. High-calcium pebble lime is slaked in a paste-type slaker to produce a 22 weight percent (wt %) slurry of calcium hydroxide (milk of lime). After screening to remove grits, the milk of lime flows to a storage tank from where it is pumped as needed to the slurry mix tank. In the mix tank, milk of lime, recycle solids, and dilution water are combined to form a 35 wt % slurry which is pumped to the slurry feed tank. Overflow from the feed tank returns to the mix tank so that the two vessels have essentially the same slurry compositions. A transport loop continuously circulates slurry from the feed tank to a head tank located above the spray-dryer atomizer and back down to the feed tank, thereby minimizing plugging problems in the lines.

The spray dryer is 7.5 m in diameter with a 5.8 m straight side and conical bottom. Dual flue-gas inlets are used with about 60% of the flue gas entering downward through the roof gas disperser and the remainder of the gas entering upward through a central disperser. The two streams meet and mix in the vicinity of the centrally located atomizer, which consists of a 21 cm (diameter) disc with eight 1 cm holes in the periphery. The disc is spun by an electric motor at 14,000 rpm to produce a fine mist of slurry droplets that react with and are dried by the flue gas. Depending on the gas flow rate, about one-fourth to one-third of the powder produced falls to the bottom of the spray dryer and is removed by a conveyor. The remainder is entrained in the gas stream and is carried to the fabric filter.

The fabric filter provides particulate-matter collection and also contributes significantly to removal of SO_2 as the flue gas passes through the dust cake on the bags (4). It is a four-compartment pulse-jet system made by the Joy Manufacturing Company. Each compartment contains 28 rows of 10 bags (each 6 in diameter x 12 ft long), giving a total filtration area of 1950 m^2 and an air-to-cloth ratio of 1.5 cm/s. The bags are of a snap-ring design and are made of 468 g woven fiberglass. Cleaning is performed off-line for one compartment at a time and is initiated on the basis of pressure drop across the baghouse. A pressure differential of about 8.9 cm H_2O is normally used to start cleaning.

The FGC system is extensively instrumented in order to support research activities as well as normal operations. The flue gas is sampled at both the system inlet and the stack using an extractive system with sample dilution at the probes. Measurements are made of SO_2 , CO_2 , NO , and NO_x (NO_2 is determined by difference) using one set of analyzers switched between the two streams. Another set of analyzers was temporarily installed for the field tests to measure the gas composition between the spray dryer and the fabric filter, and to monitor the outlet gas composition for an individual compartment of the baghouse. Gas temperatures are monitored at the spray dryer inlet and outlet, at the baghouse outlet, and at the stack. Wet- and dry-bulb temperatures are monitored at the exit from the spray dryer to measure the approach to saturation of the flue gas. Other monitors measure the pressure drop across the baghouse and across each compartment, all system flow rates, boiler conditions, and coal feed rate. All instrument outputs are recorded continuously by a computer-based data acquisition system.

FIELD TEST PROGRAM

Laboratory research has identified several sodium-based chemical additives that can enhance the NO_x -removal potential of lime ($\text{Ca}(\text{OH})_2$). Process conditions that include high spray-dryer exit temperatures, high levels of SO_2

in the flue gas, and thick filter cakes in the baghouse have also been identified as beneficial for combined removal. In addition to these laboratory results, this line of research has been spurred by reports of brown plumes (NO_2) from a western utility operating a spray dryer system that uses soda ash as the sorbent, and initial data from Niro Atomizer on the effect of caustic soda in a lime-based spray dryer for combined NO_x/SO_x removal (5). On the basis of these data, it was decided to conduct a field test of NaOH addition with elevated spray-dryer exit temperatures at a scale sufficiently large to support decisions by private industry regarding further technology development and application. An initial series of tests was conducted in August 1986 aimed at confirming the data reported by Niro Atomizer, attempting to identify the key variables associated with combined removal, and ascertaining the most favorable conditions for a combined removal process. Further tests were conducted during the spring and summer of 1988 to confirm and refine the previous results.

1986 TEST PROGRAM

Following a three-week period of baseline data acquisition under normal operating conditions, the outlet temperature from the spray dryer was increased over a one-week period in 11-degree increments from its normal value of approximately 65°C (150°F) to a final temperature of about 99°C (210°F) with no NaOH addition. This was done gradually to minimize the risk of major system upsets, but it also provided data needed to separate temperature effects from those due to the additive. Once the target temperature was reached, and the system stabilized (for about 12 hours), initial caustic injection commenced and continued for a period of two days. The addition rate was 5 wt % of the lime (as $\text{Ca}(\text{OH})_2$) addition rate. The NaOH was introduced into the slurry mix tank in a 50 wt % solution. Next, the spray-dryer outlet temperature was maintained at 99°C and the caustic addition rate was increased to 10 wt %. These conditions were maintained for approximately two more days. The final phase of the program involved a gradual reduction in the SO_2 level through a transition to low-sulfur coal. In this manner, the SO_x/NO_x ratio was decreased from nearly 6 to approximately 2. The test conditions are summarized in Table 1.

Sulfur dioxide removals were maintained between 60% and 70% throughout the test by the process control system in order to maintain compliance with the operating permit. Inlet SO_2 levels to the spray dryer were typically 1500 to 1600 ppm (corrected to 6% O_2). The only exceptions were during the final phase when SO_2 inlet levels were decreasing gradually to a low value of about 400 ppm. During that period the milk of lime and NaOH feed rates were manually held constant, giving removals that actually approached 100% near the end of the test.

Inlet NO_x levels varied between about 250 to 290 ppm (corrected to 6% O_2) during the tests. Nitrogen dioxide levels were less than 10 ppm.

Baghouse cleaning cycles were controlled as usual by the buildup of pressure across the filter. However, the lengths of the cycles were observed to vary considerably with process conditions.

During all phases of the test, significant process parameters were recorded by the data acquisition system and extensive process stream samples were taken for chemical analysis.

1988 TEST PROGRAM

Analysis of the data from the 1986 tests indicated that several areas warranted closer study. These included:

- Better definition of the temperature at which significant NO_x removal begins to occur. The lowest possible spray-dryer outlet temperature for combined removal is desirable in order to minimize lime consumption.
- The efficacy of lower rates of NaOH addition. The lowest feasible additive consumption is also economically advantageous.
- The relationship between NO_x removal and fabric filter pressure drop (cake thickness).
- Operation over longer time periods at any given condition to insure that the data represent steady state conditions.

In preparation for the tests, numerous improvements were made to the monitoring instrumentation. These changes included acquisition of a more complete and reliable set of gas analyzers for measurements between the spray dryer and the baghouse. Also, additional sampling ports were added so that the outlet gas stream from a single compartment of the baghouse could be monitored and the powder collected in that compartment could be sampled.

The test program (Table 2) was designed to investigate temperatures intermediate to those studied in 1986, to look at a lower level of NaOH addition (2.5 wt %), and to maintain each set of conditions for at least three days to allow time for the system chemistry to approach steady state through the recycle process. The experimental procedures were basically the same as those employed in 1986, except that fewer samples were taken for analysis based on the consistency seen in the earlier data. Although a total test duration of 28 days is indicated, the program actually spanned two months due to a number of boiler outages that required frequent system shutdowns. As in the earlier tests, SO_2 removals were controlled to maintain compliance with the operating permit and generally averaged about 70%. The inlet SO_2 levels were slightly higher at about 1800 ppm (6% O_2), but inlet NO_x levels were essentially the same as those in the previous tests. Baghouse cleaning cycles were again initiated on the basis of pressure drop, although adjustments to the controller were made to maximize the cycle length (and hence cake thickness) as much as possible without overloading the powder conveying system once cleaning took place.

RESULTS

EFFECTS OF TEMPERATURE

The spray-dryer outlet temperature is one of the most important variables for system performance. Normal lime-based spray-dryer operation involves outlet temperatures that are 11-22°C (20-40°F) above the adiabatic saturation temperature. For SO_2 , lower temperatures are beneficial since removals increase at a constant stoichiometry (calcium to sulfur molar ratio) as the approach to saturation decreases. However, there is no appreciable removal of NO_x at these temperatures, as shown for 68°C (155°F) in Figure 2 from the 1986 tests.

As the temperature was increased through 77°C (170°F), no noticeable change in NO_x removal was observed. Chemical analysis of the recycle powder gave nitrates and nitrites levels of about 200 ppm for each species, indicating a minor degree of removal and establishing a baseline for comparison with results from higher temperatures.

At 82°C (180°F), a dramatic transition was encountered with a very rapid increase in NO removal with temperature as shown in Figure 3. Concurrent with the increase in NO removal, a net production of NO₂ was observed. This is shown in Figure 4 for several temperatures during the 1986 tests. The NO₂ production appeared to take place in the fabric filter, as did the increased NO removal. The net effect for total NO_x was a decrease (removal), but at a somewhat lower level than that observed for NO, as shown in Figure 2.

As the temperature was increased further, the NO_x removals also increased, although the rate of increase slowed considerably above 88°C (190°F). Further evidence of the removals can be seen in the nitrates levels found in the recycle powder (Figure 5), which increased from about 200 ppm at low temperatures to approximately 4000 ppm at 99°C (210°F). The level of nitrites stayed more nearly constant, indicating the importance of NO₂ in the removal mechanism. However, attempts to use this data to achieve a material balance for nitrogen in the system have not been successful, indicating that there must exist other "sinks." This could include a reduction mechanism leading to N₂ or reactions leading to the formation of N-S compounds. This latter possibility is corroborated by the strong dependence of NO removal on SO₂ level discussed in a later section.

Changes were also noted in the properties of the powder collected in the baghouse. As shown in Table 3, increasing temperature produced a drier, more porous powder with increased surface area. From a macroscopic point of view, the changes were manifest as a reduced pressure drop through the filter cake for any given amount of powder on the bags. For example, Argonne's baghouse normally undergoes a cleaning cycle about every one and one-half hours. At a spray-dryer outlet temperature of 99°C (210°F), the interval between initiation of cleaning cycles expanded to about three hours for the same pressure drop setpoint. Note that the particulate loading had actually increased due to the increased sorbent stoichiometry required to maintain SO₂ removal.

For these tests, the stoichiometry is best expressed as an "Equivalence Ratio" (6) defined as:

$$\frac{\text{Moles of Available Calcium} + \text{Moles/2 of Sodium}}{\text{Moles of SO}_2 + \text{Moles/2 of Nitrogen Oxides}}$$

At a spray-dryer outlet temperature of 68°C (155°F) and SO₂ removal of 70%, the system internal equivalence ratio (based on both fresh sorbent feed and recycled material) was 1.02. At 88°C (190°F), the SO₂ removal had decreased (in the 1986 tests) to 58% with an internal equivalence ratio of 1.10, while at 99°C (210°F) the ratio had increased still further to 1.30 for a removal of 61%. At that point, the external equivalence ratio (based on fresh lime feed only) was about 0.9.

EFFECT OF NaOH ADDITION

The most noticeable effect from the addition of NaOH to the system was an increase in filter cake porosity (lower pressure drop) that was in addition to the increase brought about by the higher spray-dryer outlet temperatures. This

effect led to further increases in the intervals between cleanings of the baghouse. Upon addition of NaOH at the 5 wt % level, the time between cleanings increased from three to nearly six hours (Figure 6), and then to almost 8 hours when the NaOH addition was increased to 10 wt %. Analyses of the particles comprising the filter cakes indicated further changes in the surface properties of the particles beyond those produced by temperature alone, as shown in Table 3.

Nitrogen oxides removal increased with the addition of NaOH as shown in Figure 7. The effect is most dramatic at the highest temperatures, but is still appreciable even at 82°C (180°F). At 88°C (190°F), 5 wt % NaOH addition increased total NO_x removal by about 23%, while at 93°C (200°F) the increase was about 53%. Increased filter cake thickness is certainly part of the reason for the increase, but other mechanisms that have not yet been identified may also be significant.

Preliminary evaluation of the 1988 data indicates that there is little if any statistically significant improvement in NO_x removal as a result of increasing the NaOH addition rate from 2.5% to 5.0%. This is in agreement with the earlier tests, which indicated very little improvement in going from 5.0% to 10% addition. Thus, significant NO_x-removal enhancement may be possible with still lower additive levels and, hence, reduced operating costs.

FILTER-CAKE EFFECTS

Another key parameter is the thickness of filter cake that can be maintained on the bags. During the extended (6 hr) period between bag cleanings noted previously, steadily increasing removals of SO₂, NO, and NO_x were observed. A portion of that increase is shown in Figure 8. Since the buildup in the filter cake thickness is essentially an increase in the amount of available sorbent that a NO_x molecule can come into contact with while it is in the baghouse, it seems reasonable that any increases in thickness will result in an increase in the removal of NO_x, all other conditions being equal.

However, practical average removals will be less than those indicated in Figure 8 for two reasons. First, cleaning of the bags removes most of the dust cake and thereby reduces the removal rates to minimum values from which they gradually increase as more powder is collected. This gives a cyclic removal profile that closely parallels the baghouse pressure drop, as shown in Figure 9 from the 1988 tests. An average NO_x removal of about 35% was attained in those tests over an extended period. Second, the powder handling capability of the baghouse conveying system sets a practical limit on the amount of powder that can be allowed to accumulate before cleaning. In the 6 hr and 8 hr cycles noted previously, overloading of the conveyors and spillage of the powder occurred when cleaning was finally initiated. This would not be acceptable as a normal operating condition, although system hardware modifications could be made to increase the powder handling capacity if necessary.

EFFECT OF SO₂/NO_x RATIO

During the final phase of the 1986 tests, the SO₂ content of the flue gas was gradually decreased by blending in low-sulfur coal. As indicated in Figure 10, the SO₂ level in the flue gas and/or the ratio of SO₂ to NO_x has a strong influence on both NO and total NO_x removal, with the higher SO₂ levels clearly improving removals. Preliminary analysis of the 1988 data, taken at a still higher SO₂/NO_x ratio of about 6.5:1, gives average NO_x removals significantly above those seen in 1986. This is a strong indication that nitrogen-sulfur compounds of the type observed in our wet scrubbing experiments

may be a significant sink for nitrogen in the dry scrubber. Also, the system nitrogen balance could not be closed based on flue-gas composition and nitrite/nitrate levels. In this case, further research is needed to positively identify the reaction products and give an understanding of the chemical mechanism.

CONCLUSIONS

Results from the field tests indicate:

- 1) Significant removal of nitrogen oxides when the spray dryer outlet temperature exceeded 82°C (180°F). No optimum temperature or upper limit was observed in either of the tests.
- 2) A net production of NO₂ during NO_x removal.
- 3) An increase in the level of nitrates formed in the waste material (whereas the nitrites levels remained relatively constant).
- 4) An increase in the removal of NO_x proportional to the buildup of cake on the filter bags, with a subsequent loss of removal efficiency after the filters were cleaned. No significant NO_x removal was observed in the spray dryer itself.
- 5) A reduction in the removal of NO_x when flue gas with a low concentration of SO₂ was being treated by the system. This lack of NO_x removal was observed even though the concurrent SO₂ removal was well over 95%.
- 6) Enhanced removal of NO_x with the addition of NaOH to the feed slurry, primarily through creation of a more porous filter cake with more active surface area.

In summary, the potential exists for an integrated system based on spray drying that combines high levels of SO₂ and particulate-matter control with modest levels of NO_x control. The technical approach does not appear to suffer from any serious operational difficulties, but there would clearly be some economic penalties as compared to "conventional" spray drying for SO₂ removal alone. The magnitude of these costs are still under evaluation, but improvements are probable as additional research on sorbents and additives gives a better understanding of the removal mechanisms involved.

DISCLAIMER

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TABLE 1. 1986 FIELD TEST PROGRAM

Spray Dryer Exit Temp. (°C)	NaOH Addition (wt %)	Duration (days)
68	none	20*
77	none	2
88	none	2
99	none	2
99	5	2
99	10	2
99	10	2 ⁺

*Baseline characterization.

⁺Transition to low-sulfur coal.

TABLE 2. 1988 FIELD TEST PROGRAM

Spray Dryer Exit Temp. (°C)	NaOH Addition (wt %)	Duration (days)
71	none	6*
82	none	3
82	2.5	3
88	2.5	3
88	5.0	3
71	none	4*
82	5.0	3
93	5.0	3

*Baseline characterization.

TABLE 3. PROCESS CHANGES AFFECT POWDER PROPERTIES AND BAGHOUSE OPERATION

Spray Dryer Outlet Temp. (°C)	Caustic Addition (wt %)	Cleaning Interval (hr)	Powder Properties		
			Moisture (%)	Surface Area (m ² /g)	Pore Diam. Vol. Median (µm)
65	0	1.5	1.6	15.9	3.4
88	0	2.0	1.4	20.2	4.5
99	0	3.0	1.2	24.4	4.1
99	5	6.0	1.2	26.5	7.8

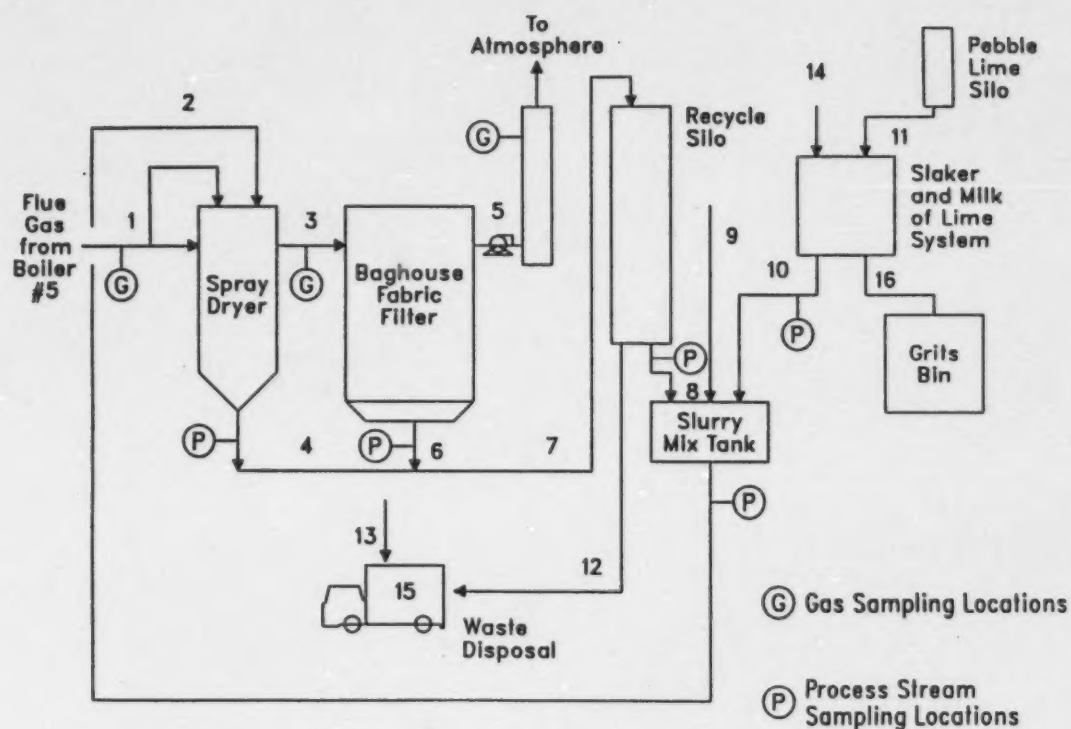


Figure 1. Process Diagram for the ANL Spray-Dryer/Fabric-Filter System

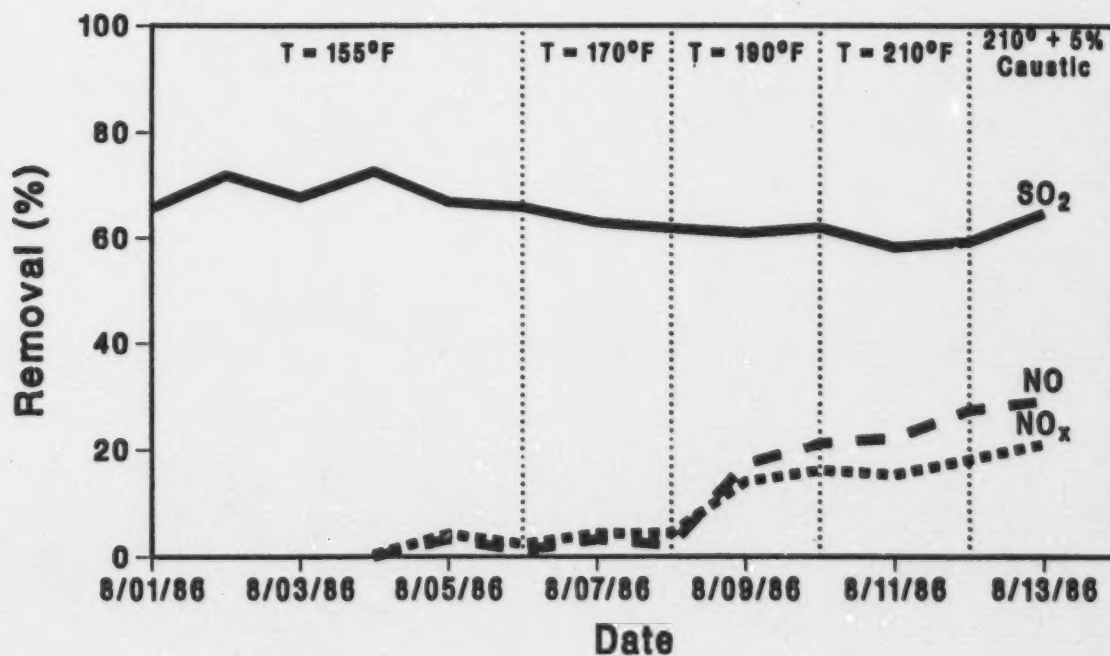


Figure 2. Spray-Dryer Outlet Temperature is Critical for Combined SO₂/NO_x Removal (1986 Tests)

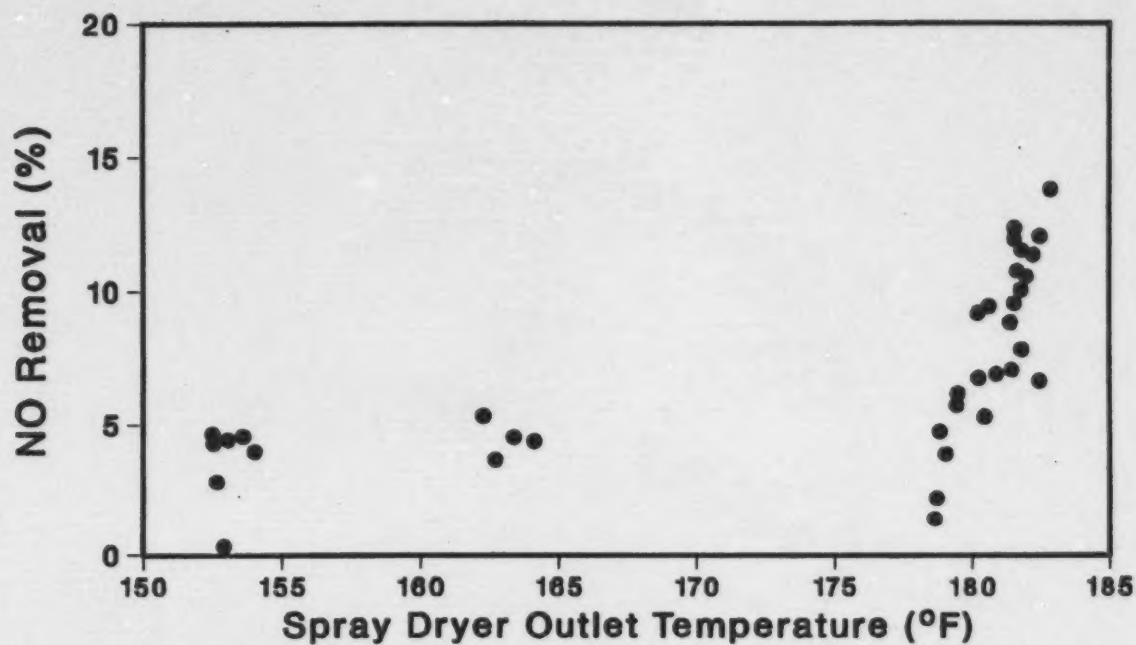


Figure 3. NO Removal Increases Sharply at about 180°F (1988 Tests)

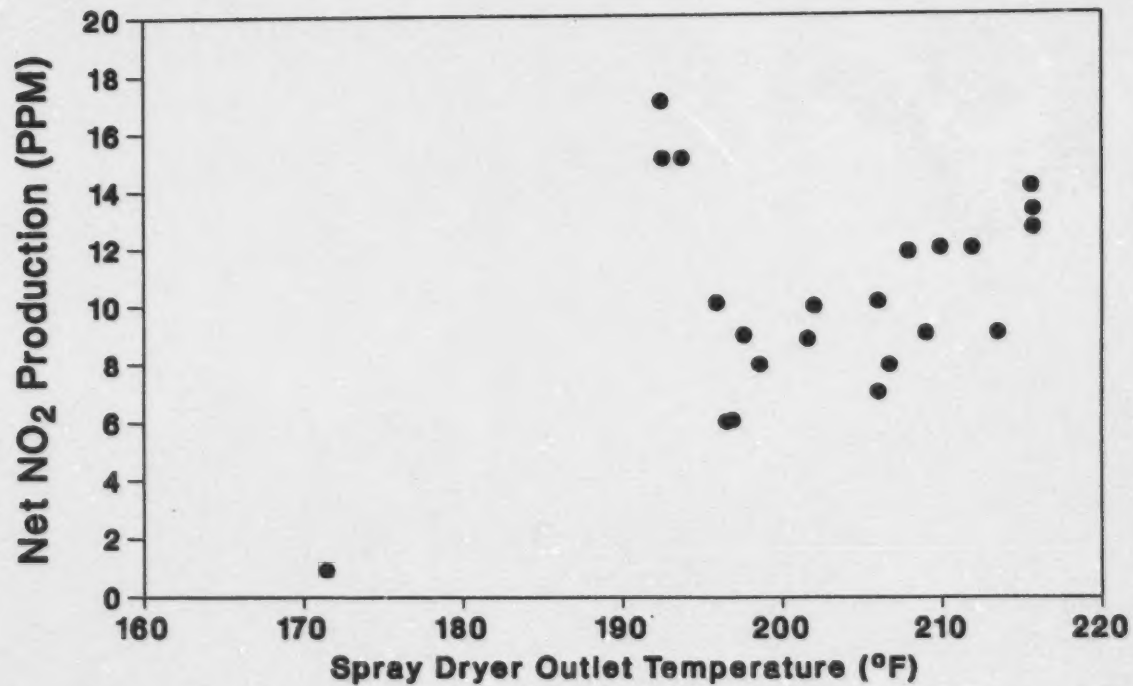


Figure 4. NO₂ Production Accompanies NO_x Removal

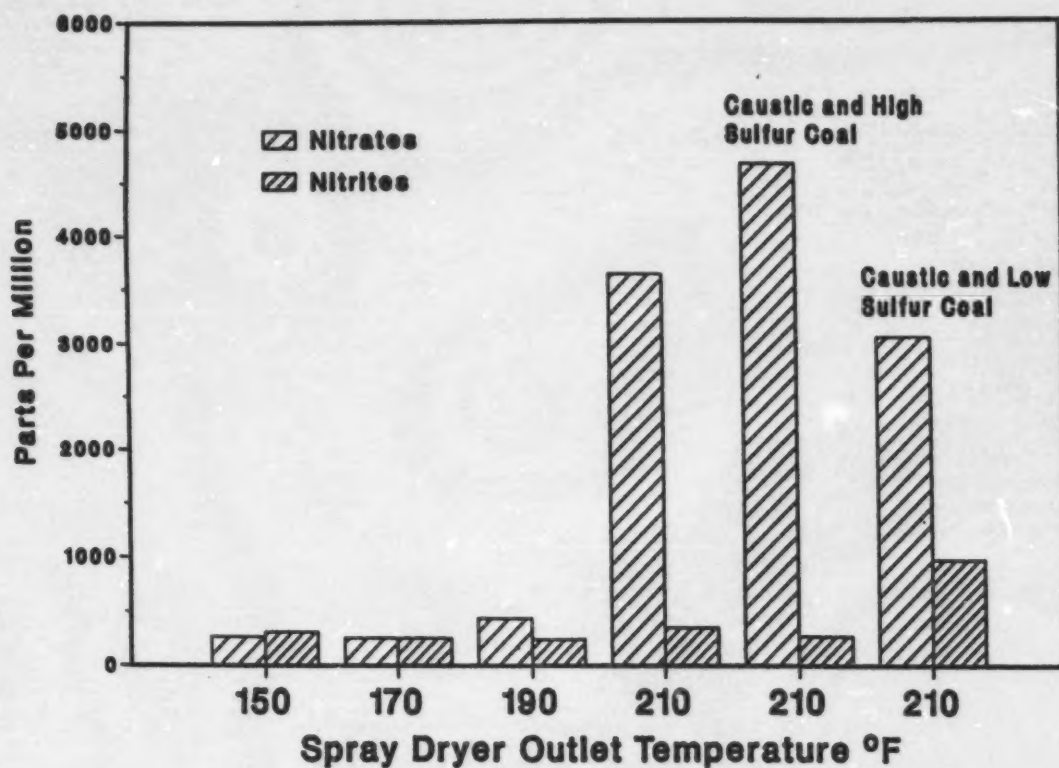


Figure 5. Concentration of Nitrites/Nitrates in the Recycle Powder Changes with NO_x Removal

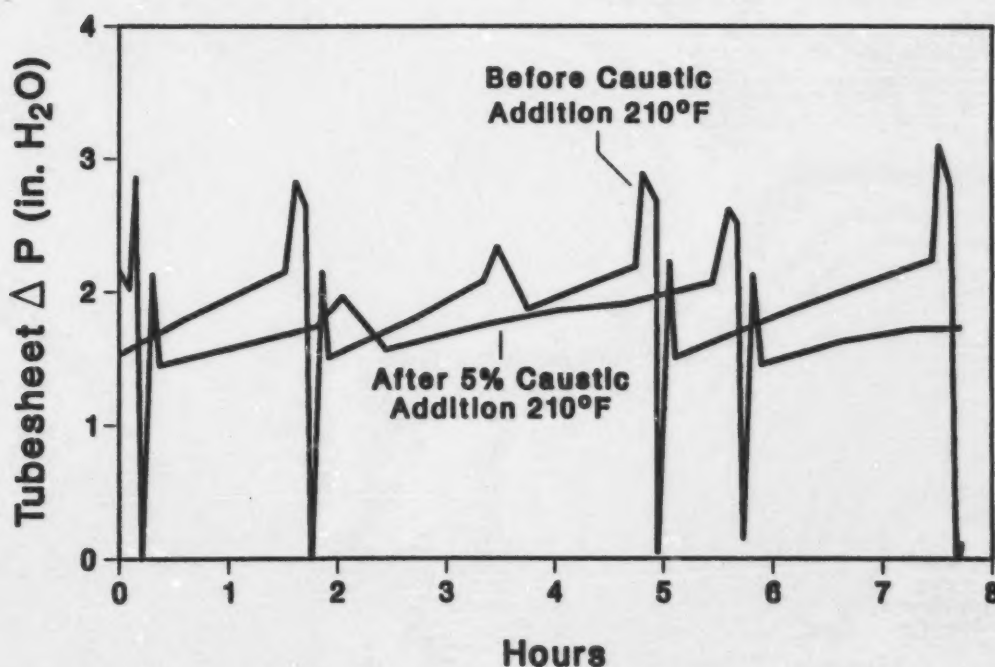


Figure 6. NaOH Addition Affects Filter Cake Properties, Allowing Longer Cycles Between Cleanings

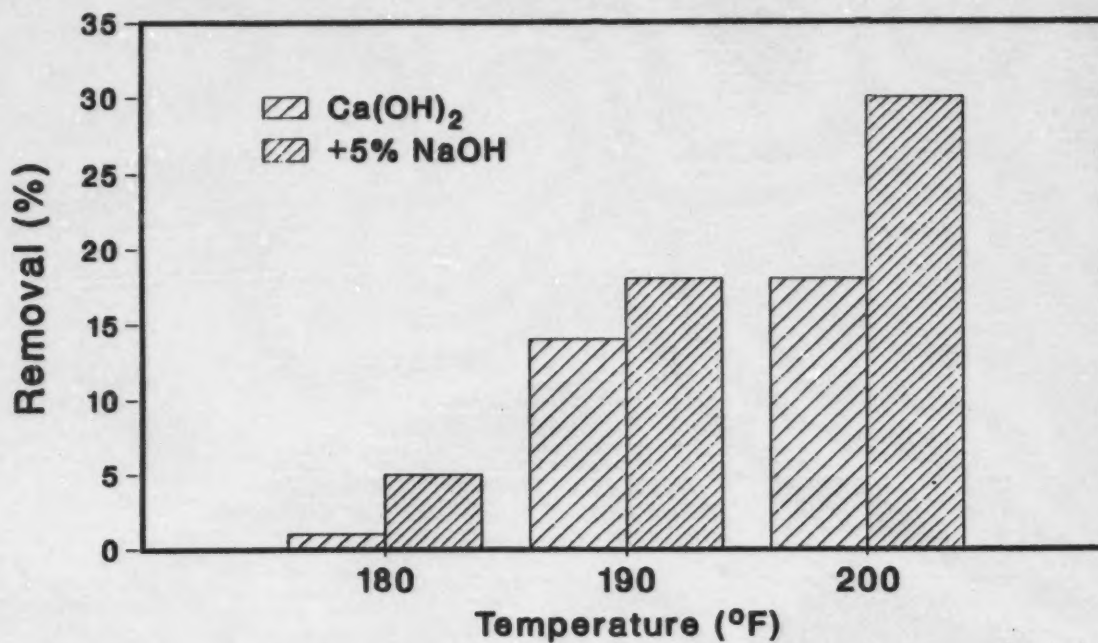


Figure 7. Additive Effects are more Significant at Higher Temperatures

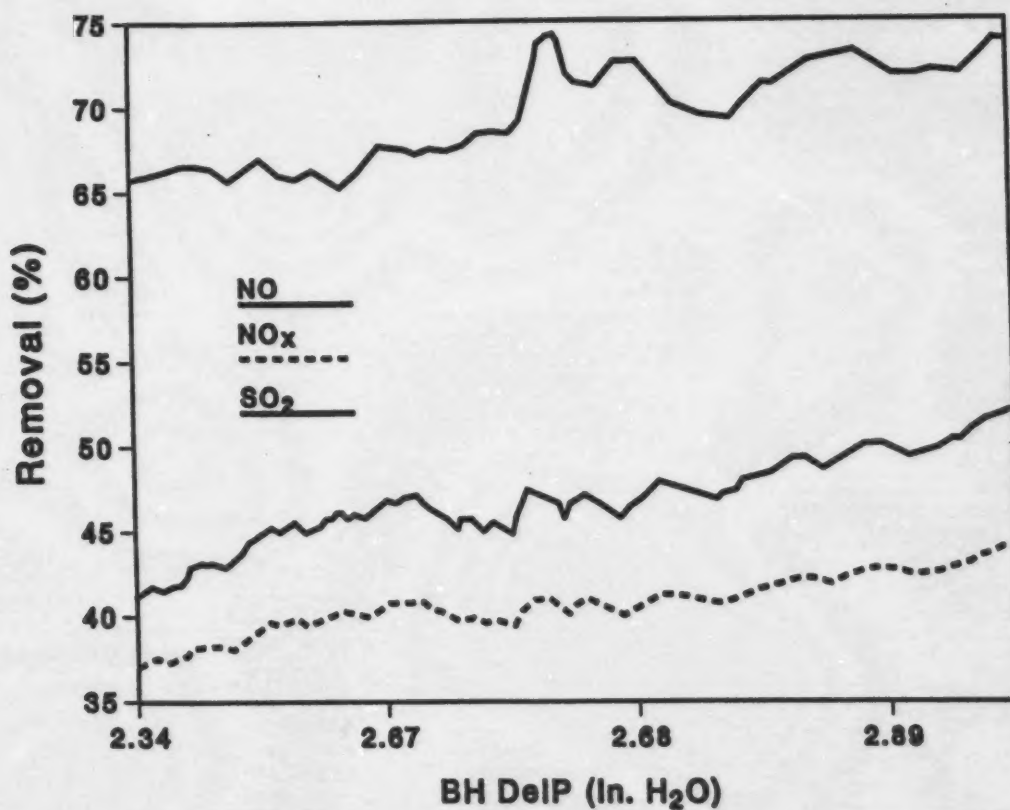


Figure 8. Removals Increase with Increasing Cake Thickness (Baghouse Pressure Drop)

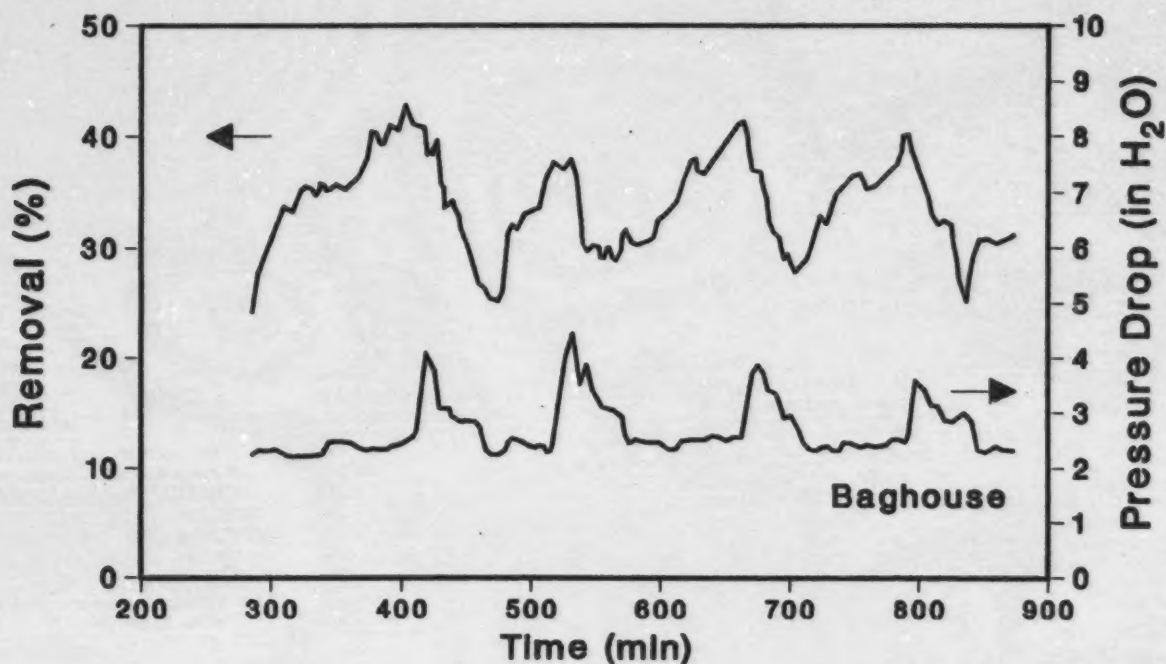


Figure 9. NO_x Removal Varies Significantly Between Baghouse Cleaning Cycles (93°C, 5 % NaOH)

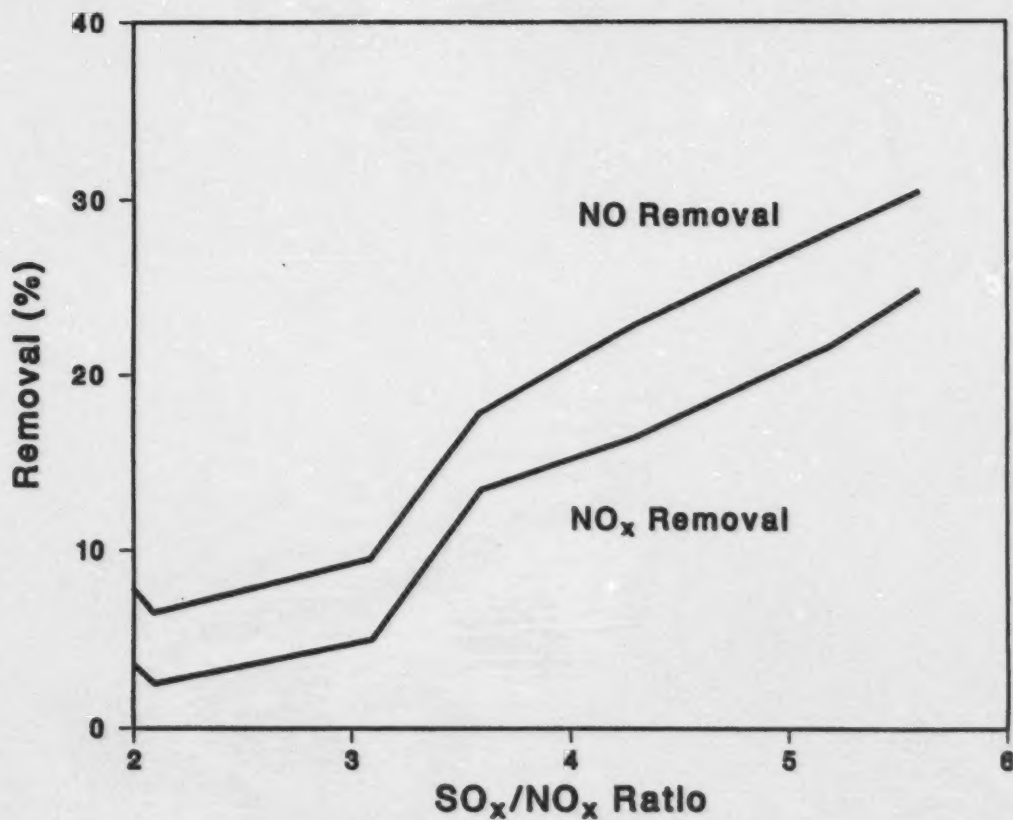


Figure 10. Sulfur Dioxide Levels Strongly Influence NO_x Removal

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First Combined FGD and Dry SO2 Control Symposium

10/25/88-10/28/88

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